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**A STUDY OF THE LONG-TERM  
WEATHERING OF SUBMERGED  
AND OVERWASHED OIL**

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# **A STUDY OF THE LONG-TERM WEATHERING OF SUBMERGED AND OVERWASHED OIL**

by

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## SUMMARY

A study is described of the long-term weathering phenomena which are experienced by heavy crude oils and residual fuels when present on a sea surface and subject to overwashing, evaporation, dissolution and photolysis. Experiments were designed and conducted to measure the increase in density of four oils (two heavy Californian crude oils, Cold Lake bitumen and a bunker fuel) as they were subjected to these weather processes. A novel experimental system for making these density measurements was devised. Experimental results were obtained and analysed. A mathematical model was developed and fitted to the data. It is concluded that the primary causes of increased density are evaporation of the more volatile and less dense components of the oil and incorporation of denser-than-water mineral matter into the oil. The effect of dissolution on density is negligible. The effect of photolysis on oil is to cause formation of a skin which retards further weathering of the "shielded" oil mass. Extensive gas chromatographic and liquid chromatographic results were obtained for the test oils. The results indicate that heavy oils, especially heavy crude oils, have the potential to achieve density increases to that of sea water. The time for this to occur under laboratory conditions can be determined relatively easily and is typically 10 days. Relating this laboratory exposure time to oceanic exposure time is difficult, it being suspected that it may take, for example, 30 days at the ocean surface for an equivalent density increase to occur. Much spilled heavy oil may eventually sink, but is unlikely to be observed to do so because of the long times. It is believed that the mathematical model will assist in the elucidation of the conditions under which heavy oils become subject to permanent sinking in the marine environment, especially if it can be linked to an oil spill behaviour model which takes into account the phenomena of overwashing and partial or periodic oil mass submergence.

## RÉSUMÉ

On décrit des travaux portant sur les phénomènes de transformation à long terme des bruts lourds et des fuels résiduels en surface d'eau de mer et exposés à l'ennoiement, à l'évaporation, à la dissolution et à la photolyse. On a fait des expériences visant à mesurer l'augmentation en densité de quatre pétroles (deux bruts lourds californiens, un bitume de Cold Lake, un fuel de soute) qui étaient soumis à ces processus d'altération. On a conçu un système expérimental de mesure de la densité. On a obtenu des résultats expérimentaux et on les a analysés. Un modèle mathématique a été calculé et ajusté aux données. Il est conclu que les principales causes de l'augmentation de densité sont l'évaporation de la fraction la plus volatile et la moins dense du pétrole et l'incorporation dans l'huile de matières minérales plus denses que l'eau. La dissolution a un effet négligeable sur la densité. La photolyse conduit à la formation d'une pellicule qui retarde l'altération subséquente du pétrole recouvert. On a procédé à des chromatographies extensives en phase gazeuse et en phase liquide sur les pétroles essayés. Le résultat indique que les huiles lourdes, notamment les bruts, peuvent finir par atteindre la densité de l'eau de mer. En laboratoire, il est relativement facile de déterminer la période nécessaire à cela, normalement dix jours. Il est cependant difficile d'établir un lien entre cette mesure et la durée d'exposition nécessaire en mer; en effet, on suspecte, par exemple, que le pétrole peut mettre trente jours en surface de la mer avant de parvenir à cette même densité. Une bonne partie du pétrole lourd qui serait déversé finirait éventuellement par couler, mais il est peu probable qu'on puisse observer ce phénomène étant donné les longues périodes en cause. On pense que le modèle mathématique contribuera à élucider dans quelles conditions les huiles lourdes sont sujettes à couler de manière permanente dans un milieu marin, notamment si le modèle peut être relié à un modèle de comportement des nappes qui tient compte des phénomènes d'ennoiement et de submergence partielle ou périodique de la nappe.

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## 1. INTRODUCTION

### 1.1 The Phenomenon of Sinking

Conventional oils and petroleum products when spilled in the marine environment almost invariably float on the water surface and are subject to a number of processes including evaporation, dissolution and photolysis, formation of oil-in-water emulsions and water-in-oil emulsions, these processes being collectively termed "weathering". A considerable number of studies has been undertaken of the rates of these processes, and mathematical models have been developed describing and predicting these rates, and the effects these processes have on oil properties (Mackay and McAuliffe, 1988). Generally, the oil becomes denser because of evaporation of the less dense, volatile hydrocarbons but the density rarely increases to that of water i.e.  $1000 \text{ kg/m}^3$  in freshwater or approximately  $1024 \text{ kg/m}^3$  in marine water. It is of concern, however, that certain heavy crude oils and residual products such as Bunker C which have densities exceeding  $900 \text{ kg/m}^3$  could increase in density to the extent that they become denser than water and become subject to sinking. This could lead to a significant environmental impact because the sensitive and often economically valuable benthic environment could become contaminated by masses of sunken oil. The implications for lobster or shell fisheries are obvious. It is therefore prudent to ascertain if these oils can become denser than seawater, and if so, what conditions will cause this phenomenon.

Previous studies by Wilson et al. (1986), Clark et al. (1987), Ross (1987) and Buist and Potter (1987) have shown that the sinking phenomenon is not simply one of negative buoyancy. When an oil mass is weathered and the density approaches that of water it sinks more deeply into the water and becomes subject to appreciable overwashing as the result of wave and current actions in the near-surface region. The oil may in fact spend an appreciable fraction of its history underwater being conveyed in near-surface currents by large eddies. It may thus be invisible to observers at the sea surface, or to remote sensing systems. Several incidents have occurred in which there has been anecdotal evidence that oil masses have submerged, only to reappear at distant locations on the water surface. It appears that oil masses which have densities close to that of sea water have "Stokes Law" rising velocities (acknowledging that Stokes Law will probably not apply under turbulent conditions experienced at the ocean surface) which are less than the velocities of eddies which exist as a result of wind, wave and current action in the near-surface

region. The oil may thus be subject to appreciable periods of submergence. In many respects the phenomenon is analogous to that of aerosol particles in the atmosphere which are eventually deposited on land or water surfaces by a dry deposition velocity, but which experience a long history of movement in the atmospheric turbulence fields prior to deposition.

Five processes may contribute to an increase in oil density.

1. Evaporation

Evaporation tends to remove from the oil the more volatile hydrocarbons which also tend to be the less dense chemical species. Accordingly, the residue will show an increase in density. This process is fairly well quantified for light oils, however, for heavy oils the rate at which evaporation occurs is not well understood largely because the oils are so involatile. It is not known, for example, if evaporation will result in a significant density increase in any reasonable exposure time.

2. Dissolution

Oil or oil components are subject to dissolution, particularly as a result of overwashing by wave action. Again the more soluble hydrocarbons will preferentially dissolve. These tend to be the lower molecular weight species, and especially the lower molecular weight aromatics. The preferential dissolution of these less dense chemicals may result in an increase in oil density. Again the magnitude of this effect, and the rate of the process, are not known.

3. Photolysis

Oil is subject to photolysis as a result of absorption of photons from sunlight. Photolytic processes can result in polymerization to form denser, higher molecular weight species. Photolysis may also cause the formation of free radicals which are susceptible to oxidation resulting in the formation of oxygenated species as peroxy and hydroxyl radicals, alcohols, ketones, carboxylic acids and aldehydes. Generally, these polar oxygenated species are considerably more water soluble than the parent hydrocarbons. They are also denser than the hydrocarbons, for example, tetradecane has a density of  $765 \text{ kg/m}^3$  whereas tetradecanol

has a density of  $836 \text{ kg/m}^3$  (Weast, 1975). The rates at which polymeric or oxygenated species are formed are not well established but there is a widely held belief that the effects of photolysis are generally underestimated and the general role of photolysis as a weathering process is underappreciated, from both oil fate and toxicity viewpoints. There are few studies of crude oil photolysis, recent careful studies being that of Lichtenthaler et al. (1988) and Bobra (1989).

#### 4. Attachment of foreign matter

The oil mass undoubtedly comes into contact with mineral matter such as diatomaceous material and biota which may become attached to the oil, or become incorporated into it, resulting in an increase in density. This process has been observed and reported by Wong et al. (1984) and may be responsible for oil sinking especially in areas of high suspended solids content, for example in relatively shallow near-shore waters, estuaries or during storms. No satisfactory description of the kinetics of the uptake of solid matter by an oil mass is available, however, it seems likely that interfacial phenomena play an important role in determining the extent to which attachment occurs. Over prolonged periods of time (i.e. many days) it is likely that bacterial slimes will accumulate on the oil surface since the waters immediately adjacent to the oil surface are rich carbon sources. Again the effect on density is unknown. This phenomenon has also been discussed by Meyers (1972) and Meyers and Oas (1978), but mainly for sorbed hydrocarbons.

One situation in which this process is very important occurs when viscous oil masses drift into the breaking wave region close to sandy shores. The oil drops, which may range from a few millimetres to a few centimetres in diameter may pick up sand particles, thus becoming denser. Eventually they may become incorporated into the beach, or if the tide is receding, they may drift out to sea and become partially or totally submerged, or sink to the bottom. Evidence was obtained from the "Nestucca" barge spill off the BC coast in late 1988 to the effect that collected oil contained an appreciable sand content and thus had been subject to this process (Fingas-personal communication, 1989).

It should also be noted that much foreign matter at the sea surface is less dense than water, examples being organic debris. Attachment of such matter to oil will, of course, enhance floating and reduces the probability of sinking.

## 5. Water uptake

Finally, it is likely that most oils incorporate water both by dissolution and formation of water-in-oil emulsions thus causing an increase in oil density. In some cases, in which the oils contain emulsion-stabilizing species, water volumetric contents as high 80 to 90% have been observed. These "mousses" have densities very close to that of the water which is incorporated in the oil mass, but in theory it is impossible for such emulsions to achieve a higher density than water (Mackay, 1987).

As part of this project, an extensive survey was undertaken and contact was made with numerous agencies in an attempt to ascertain the current state-of-the-art in this area, and the presence of related research programs. No relevant research programs were found. The most relevant work has been sponsored by Environment Canada through the Arctic and Marine Oilspill Program, and reported at its annual meetings and published in the Proceedings. A list of relevant reports and papers is given in the References and Bibliography sections of this report, and they are referred to in the body of this text when appropriate.

It is believed that as a result of the "Nestucca" barge collision off the Washington State coast in December 1988, a number of research and investigative efforts into this phenomenon are now being undertaken but it is too early to comment on results.

## 1.2 The Experimental Approach

A laboratory research program was designed in an attempt to obtain measurements of density increases over periods of approximately 20 days, of oils exposed to various weathering regimes including evaporation, dissolution, contact with solid materials and microbiota and photolysis. It was decided to use four oils of relatively high density and high viscosity. These were Cold Lake Bitumen (CLB), California Crude Oil API 11 (C11), Bunker C Fuel Oil (BC) and California Crude Oil API 15 (C15). These oils were subjected to physical-chemical property determinations and analysis by gas chromatography. A program of exploratory research was then undertaken in an attempt to devise a system in which oils could be exposed to various weathering regimes and the density increases monitored using a relatively non-disturbing technique. This proved to be difficult, but after some trial and error an exposure measurement system was devised which it is believed gives as good results as is possible with the present state of knowledge and resources. The system

which was devised and used is described in detail in Chapter 2. Considerable effort was devoted to improving the precision and accuracy of the measurements. A mathematical model is developed in Chapter 3 to express or "fit" and correlate the density increases in a quantitative manner. The experimental results obtained are described in Chapter 4 and are fitted to the model. The combination of results, model and fitting is an equation for density variation with time which contains a minimum number of adjustable parameters which describes satisfactorily the observed experimental data. With appropriate caution the equation can be used to predict density increases of oils in marine environmental conditions. As is noted later the equations should be applied with particular caution to other crude oils because compositions vary and these oils may be subject to somewhat different process rates. In cases where it is important to ascertain the sinking characteristics of a specific oil, the work described here should be regarded as contributing to a protocol which can be followed by other investigators to characterize density characteristics of that oil under the particular prevailing marine environmental conditions. Finally in Chapter 5 conclusions derived from this work are outlined and recommendations are made for future studies.

## 2. EXPERIMENTAL

### 2.1 Materials

The four oils tested supplied by Environment Canada and the US Minerals Management Service are listed along with appropriate physical-chemical properties in Table 2.1. This table contains data kindly provided by M. Bobra working under contract to Environment Canada. It is notable that they cover a fairly wide range in densities and viscosities. The four oils were analyzed by gas chromatography and their chromatograms are shown in Figures 2.1 to 2.4. Table 2.2 gives information on the composition of these oils obtained by open column liquid chromatography under the defined conditions. Gas chromatograms were also obtained for various fractions and are shown in Figures 2.5 to 2.8. The oils were contacted with double distilled water and salt water consisting of 32 parts per thousand sodium chloride (NaCl) and the water soluble fraction subjected to analysis as shown in Table 2.3. The most readily measured compounds were benzene, toluene, ethylbenzene, xylenes, and naphthalene (Figures 2.9 to 2.12) because they can be determined accurately by head space or purge and trap analyses. California Crude 15 showed the presence of appreciable concentrations of these chemicals having a total water solubility of approximately 26 mg/L in freshwater and 15 mg/L in salt water. Since the average solubility of these hydrocarbons is some 400 mg/L, it appears that this oil contains a mole fraction of these fairly soluble hydrocarbons amounting to 25/400 or 0.06 or approximately 6%. California Crude 11 had approximately half of this quantity. The Bunker C Fuel Oil had a very low concentration of aromatics presumably as a result of extensive distillation. Cold Lake Bitumen had only negligible contents of lower aromatics. It is therefore expected that the California crude oils will behave quite differently from the fuel oil and Cold Lake bitumen when exposed to evaporation and dissolution conditions.

### 2.2 Density Determination

The system eventually adopted for exposure and density determination is illustrated in Figure 2.13. Disks were obtained of polyester mesh of diameter 6 cm made from PeCap® polyester manufactured by Tetko Inc. This mesh has an opening of 0.5 mm and a filament diameter of 0.3 mm. A number of mesh sizes and thread diameters were tested, however, this combination was found to be most suitable in that the oil was well retained by the mesh with a minimum of



"dripping". Plastic mesh is preferable to metallic mesh because of its lower density. Some properties of these meshes are given in Table 2.4. The meshes are used for filtering and printing purposes.

The approach used to determine densities was basically the Archimedean principle of weighing the oil mass in air and in water, the difference being the buoyancy induced by displacement of the volume of water. Corrections were introduced for the presence of the mesh. The equation used (in units of kg and m<sup>3</sup>) was:

$$\text{Density of oil } D_o = \text{Mass of oil } M_o / \text{Volume of oil } V_o$$

where

$$M_o = M_T - M_M$$

where  $M_T$  is the mass of oil plus mesh in air and  $M_M$  is the mass of the mesh,

and

$$V_o = V_T - V_M$$

where  $V_T$  is the total volume of oil plus mesh and is calculated from

$$V_T = (M_T - M_{TS}) / D_w$$

where  $M_{TS}$  is the apparent mass or weight of the submerged oil plus mesh and  $D_w$  is the density of the water.  $(M_T - M_{TS})$  is thus the buoyancy induced by the water.

$V_M$  is the volume of the mesh which was determined by weighing the mesh in air and water. It was found that the calculated density of the mesh (i.e.  $M_M / V_M$ ) agreed with the density published by the manufacturer of 1380 kg/m<sup>3</sup>.

Care was taken to remove all air bubbles from the oil and mesh during weighing in water and to minimize surface tension effects on the suspending filament. In the early stages of the work considerable effort was devoted to improving technique, accuracy and precision.

Usually, 0.5 to 1.0 g of oil was coated on to a mesh disk of 60 mm diameter with heat-sealed edges. This gave a reproducible and controlled area/volume ratio.

Table 2.1 Properties of Crude Oils and Residual Fuels

Property	California Crude API 15	Bunker C fuel oil	California crude API 11	Cold Lake Bitumen	Temp. (°C)	Reference
API Gravity	13.2	12.3	10.3	9.8	20	Environment Canada
Density (g/cm <sup>3</sup> )	0.9907	0.9941	0.9968	1.0075	0	EC
	0.9832	0.9904	0.9942	1.0049	5	EC
	0.9802	0.9867	0.9915	1.0023	10	EC
	0.9770	0.9830	0.9882	1.0002	15	EC
	0.9735	0.9788	0.9852	0.9968	20	EC
	0.9681	0.9712	0.9779	0.9851	22±2	this work
	0.9702	0.9749	0.9824	0.9943	25	EC
	0.9672	0.9718	0.9796	0.9916	30	EC
Viscosity (cp)	6.4e3	1.4e6	2.2e5	>3.0e6	0	EC
	3.1e4	4.8e4	3.4e4	2.4e5	15	EC
Solubility (mg/L) d.d.H <sub>2</sub> O	25.7	4.23	11.3	0.26	22±2	this work
Salt H <sub>2</sub> O*	14.7	1.95	9.74	0.13	22±2	this work

\* 3.0 wt % NaCl in salt water.

Table 2.2 Hydrocarbon Analysis by Open Column Chromatography

Composition	weight %			
	California crude API 15	California crude API 11	Cold Lake Bitumen	Bunker C fuel oil
Saturates	13.7	13.7	16.6	31.3
Aromatics	36.4	29.8	39.2	45.7
Asphaltenes	25.8	24.8	19.3	10.8
NSO compounds	24.1	31.7	24.9	12.2

Table 2.3 Major Components of WSFs of crude oils at 22°C

		solubility, mg/L				
Oil		Benzene	Toluene	Ethylbenzene xylenes	Napthalene	Total
California crude API 15.0	d.d.H <sub>2</sub> O	8.35	4.84	2.83	0.06	25.7
	salt H <sub>2</sub> O	4.86	2.57	1.62	0.043	14.7
California crude API 11.0	d.d.H <sub>2</sub> O	1.4	0.825	2.33	0.077	11.33
	salt H <sub>2</sub> O	0.786	0.438	1.09	0.037	9.74
Bunker C fuel oil	d.d.H <sub>2</sub> O	0.428	0.771	1.02	0.091	4.23
	salt H <sub>2</sub> O	0.209	0.371	0.384	0.03	1.95
Cold Lake Bitumen	d.d.H <sub>2</sub> O	0.009	0.02	0.035	0.006	0.26
	salt H <sub>2</sub> O	0.0024	0.014	0.016	0.004	0.13

Table 2.4 Physical and Chemical Properties of PeCap® Polyester Mesh\*

Property	
Melting Point (°C)	250 - 260
Softening Point (°C)	220 - 240
Specific Gravity	1.38
% Moisture Absorption 20°C. 65% Relative Humidity	0.4
Mesh Opening (microns)	500
Open Area (%)	39
Mesh Count Per Inch	32
Thread Diameter (microns)	300
Fabric Thickness (microns)	650
Chemical Resistance to Petroleum Hydrocarbons	satisfactorily resistant to benzene, carbon tetrachloride, hexane, toluene, etc.

\* data provided by Tetko® Inc, supplier B&SH Thompson & Co. Ltd, 140 Midwest Road, Scarborough, Ontario M1P 3B3.

The results presented in the next section are generally of these computed densities and represent the average of six determinations using separate sections of oiled mesh.

### 2.3 Gas Chromatography

A Hewlett-Packard GC model 5700A equipped with a flame-ionization detector was used to analyze fresh and weathered samples of oil obtained from the oil weathering experiments. The column was a 0.075 cm ID x 50 m long glass capillary column coated with SE-30 (Supelco Canada, Ltd.). The operating conditions were: the initial oven temperature was 50°C for 8 minutes and the oven temperature was programmed to 250°C at a rate of 5°C/min. The injection sample had a volume of 0.5  $\mu$ L with a split ratio of 50:1, and the peak areas were recorded with a Shimadzu Chromatopac C-R1A integrator using the area normalization method.

### 2.4 Column Chromatography

Approximately 1.5 g of oil was diluted in 100 mL of n-pentane. The mixture was filtered through a pre-weighed filter to remove the asphaltene content. The filter was dried in a heating compartment for 24 hours before being weighed again to determine the percentage weight of asphaltene.

The de-asphalted oil was separated into three fractions: saturates, aromatics and polar compounds using the procedure described by Cook and Westlake (1976). A dual-phase column packed with 1:1 ratio of silica gel and alumina was used. The silica gel (28-200 mesh) and alumina (type F-20, 80-200 mesh) were supplied by Sigma Chemical Co. The order of elution was as follows: saturates with pentane, aromatics with benzene, and then soluble polar compounds with a 1:1 mixture of benzene-methanol. The collected fractions were concentrated by evaporation of the solvent and later weighed to obtain the percentage composition of each fraction in the crude oils. However, some of the volatile compounds in the oils evaporated along with the solvent and therefore, errors were introduced into the calculation of the oil compositions.

### 2.5 Liquid Chromatography

Another method used for the separation of the de-asphalted oil into the three fractions was normal phase liquid chromatography. The HPLC system used was composed of a Waters Scientific

model 510EF solvent delivery system, an U6K injector with a 2-mL sample loop, a 6-part backflush valve, and a model 401 differential refractometer. n-pentane of HPLC grade (supplied by Caledon Laboratories) was the mobile phase. Two different columns can be used. One is a semi-preparative 2.5 cm I.D.X. 30 cm long stainless steel column packed with dry  $\text{NH}_2$  Bondapak which is used to fractionate the oil. Each fraction is collected and quantified gravimetrically. The second column is an analytical column. With the use of the latter column, a calibration has to be performed on the HPLC refractometer to determine its response to the different fractions. However, there is uncertainty in the choice of an oil as the calibration standard. The peak areas were recorded with a HP-3390 integrator.

With the semi-preparative column, samples of 100  $\mu\text{L}$  were injected into the system and the fractions eluted with a flowrate of 18.0 mL/min. For the elution of polar compounds, the flow through the column was reversed by backflush. The collected fractions were concentrated using a micro-distillation apparatus, and placed into pre-weighed 1.5-mL screw cap septum vials for quantification of the composition of the crude oils.

## 2.6 Aqueous Solubility

Aqueous solubilities of the crude oils in double-distilled water and salt water (3 wt% NaCl) were determined at  $22 \pm 2^\circ\text{C}$  by purge-and-trap chromatography analysis.

Saturated solutions of the crude oils were prepared by adding 10 mL to 50-100 mL of water in a 125-mL separatory funnel. The volume ratio of oil to water should exceed 1:40. The separatory funnels were shaken gently with a wrist-action shaker for a period of 24 hours, and the oil mixture was allowed to settle for at least 48 hours before analysis.

Analysis of the saturated solutions were performed with a Hewlett-Packard model 5840A GC with a flame-ionization detector and a HP-7675A purge-and-trap sampler. The column was a 0.53 mm ID x 30 m long mega bore fused silica capillary column coated with DB-1 (J&W Scientific, Inc.) The operating conditions were as follows: the initial oven temperature was  $50^\circ\text{C}$  for 10 minutes with a temperature programming rate of  $5^\circ\text{C}/\text{min}$ , and the final oven temperature was  $200^\circ\text{C}$  for 20 minutes. The detector temperature was set at  $300^\circ\text{C}$ . The peak areas were integrated using a HP-5840A GC terminal. The sample volume used ranged from 2 mL to 12 mL for the least water-soluble crude oil.

## 2.7 Oil Weathering Experimental Design

The following weathering experiments were conducted on the four crude oils:

- evaporation in the fumehood in the dark,
- evaporation in the fumehood with photolytic exposure,
- dissolution in a continuous flow of distilled water,
- dissolution in salt water,
- biodegradation,
- contact with suspended inorganic particles, and
- dissolution with photolytic exposure.

### Evaporation

From initial tests, it was found that only a small fraction of oil (up to 20%) was retained on the disk when it was held stationary in air; therefore, a rotating device was devised which rotated (at a rate of 1.0 rpm) the oil-covered disks continuously between a horizontal and a vertical position. However, there was a small possibility of oil dripping off the disks during the first few days. The apparatus was placed in a fumehood that had a fairly high air flow. Two runs of the evaporation experiment were performed for 3 to 4 weeks with one at 19-20°C and the other at 22-24°C. Density measurements were taken after, 6, 24, 48, and 72 hours from the initial exposure for the second run because the greatest changes in density occur during the initial evaporation period.

The remaining experiments were conducted at 20°C  $\pm$  2°C.

### Photolysis in Air

The source for photolysis was two fluorescent UVA-340 40-watt lamps, kindly supplied by Environment Canada, which were mounted on standard light fixtures in the fumehood. The 48 inch fluorescent tubes were obtained from the Q-Panel Company. The lamp's emission was in the UV-A region with a small amount of UV-B. This is believed to be a satisfactory simulation of sunlight in the critical short wavelength UV region in the range 365 nm to 295 nm.

Oil samples on the disks were again circulated vertically on a rotating device.

### Dissolution

Stainless steel hooks attached on to glass rods were used to hang oil-covered mesh disks vertically into a tank containing 27 L of distilled water. The disks were spaced apart at a distance of 2.5 cm. A constant daily flowrate of water was maintained with inflow of fresh water supplied by an overhead cylindrical tank. The disks were rotated 90° from the original position every two days for the first two weeks to prevent the oil from flowing off the disks and creating a slick on the water surface. Approximately 1.0 g of oil per disk was applied.

A second dissolution experiment used salt water instead of distilled water. Instant Ocean<sup>®</sup> (manufactured by Aquarium Systems) was used to provide the salt content which approximately simulates that found in sea water. Only 0.5 g of the oil was applied on each disk because of the high tendency for the oil to separate from the disk and float to the water surface. Half of the 7.5 L salt water was replaced weekly with a freshly-made solution of equal density.

Density measurements for both dissolution experiments were made weekly. However, before the densities of the oils could be determined, the oil-disks were dried on a rotating device in the fumehood. Inevitably this resulted in some evaporation.

### Photolysis in Water

This apparatus was similar to the dissolution experiment except for the additional use of sunlight-simulation lamps. The UVA-340 lamps were angled such that more ultra-violet light was received by one side of the glass tank. After each weekly measurement, the disks from the two different sides were manually interchanged so that each oil had the same light exposure.

### Exposure to Micro-Organisms

Fresh lake water (24 L) containing microorganisms was obtained from Lake Ontario for exposure to the crude oils. It was found necessary to add P and N to the water so that the microbial population was maintained. This was accomplished with  $3.5 \times 10^{-5}$  of sodium phosphate dibasic  $\text{Na}_2\text{HPO}_4$  (from Fisher Scientific Co.) and  $10^{-2}$  M potassium nitrate  $\text{KNO}_3$  (from BDH, analytical

reagent). Water conditions were stagnant in the tank, which had a total volume approximately of 31.2 L.

### Contact with Inorganic Particles

In the initial experiments purified bentonite powder (supplied by Fisher Scientific Co.) of 0.1 wt% in distilled water was used to expose the crude oils to suspended mineral matter. This mixture had to be continuously stirred at a moderate speed to produce a uniform suspension of particles throughout the 7.5-L tank. High stirring speeds caused the oil-coated disks to collide with each other.

Before the oil densities can be determined, the disks were initially immersed in distilled water in an attempt to displace the bentonite particles from the exposed mesh openings. The oil covered disks were then dried on the rotating device for about 40 minutes.

After these initial experiments a more comprehensive series of experiments was undertaken exposing the oils to a series of mineral materials of density  $D$  kg/m<sup>3</sup> as follows

- Pottery clay purchased from a local hobby shop ( $D = 2240$ )
- Riverbed clay obtained from a river near Whitevale, Ontario ( $D = 2510$ )
- Kaolinite obtained from the Geology Department, University of Toronto ( $D = 2680$ )
- Diatomaceous Earth (Fisher) ( $D = 2150$ )
- Soapstone, i.e. talc, obtained by grinding a piece of soapstone obtained at a hobby shop for carving purposes ( $D = 2620$ )

Soapstone was used because it is reputed to be very "hydrophobic" and may thus be unusually susceptible to oil attachment.

### Weathered Oil Sample Analyses

Samples of Heavy California crude oil API 15 coated on disks were taken from the following experiments: evaporation, dissolution in fresh water, photolysis in air, and biodegradation. They were sampled in accordance with the density determination measurements. The oil was extracted from the disks with n-pentane. The extraction was aided by the use of a bath with ultrasonic



vibration which caused the oil to be released from the disk and be dissolved in the n-pentane. The excess n-pentane was evaporated from the resulting mixture by micro-distillation at 40°C. The concentrated samples were pipetted into 7.0-mL vials and stored at 4°C for later analysis by gas chromatography so that changes in chemical composition of the crude oil attributed to the above processes can be observed over time.

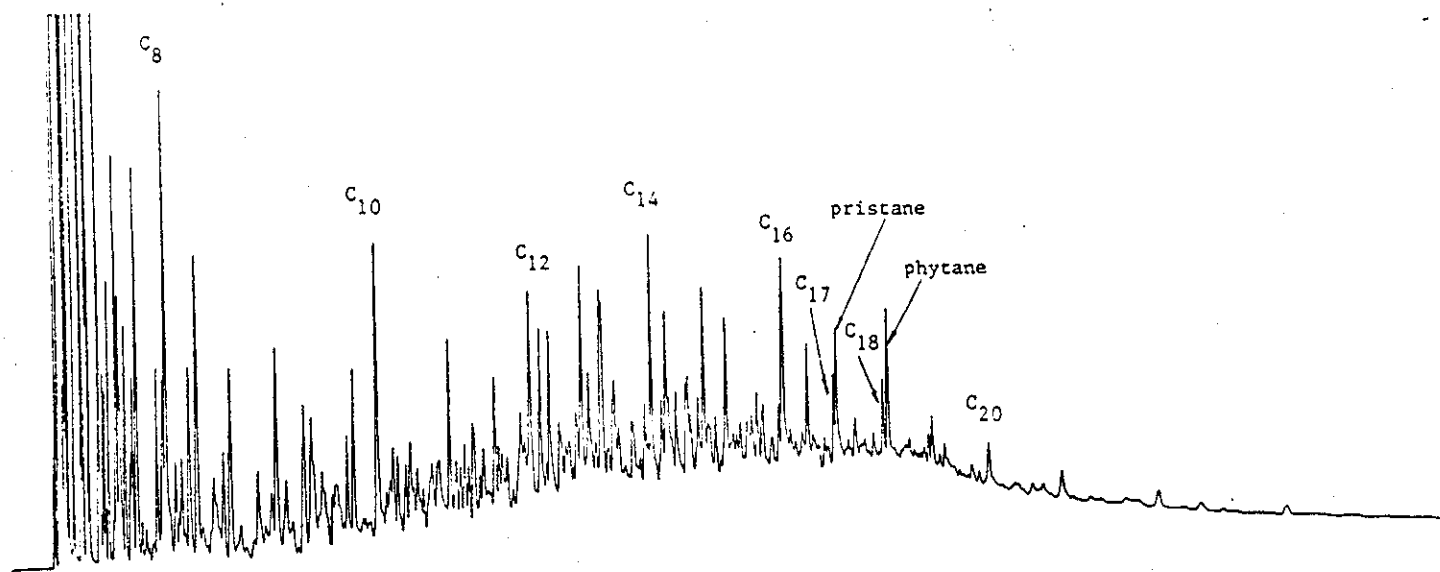


Figure 2.1 Gas chromatogram of fresh California Crude Oil API 15.

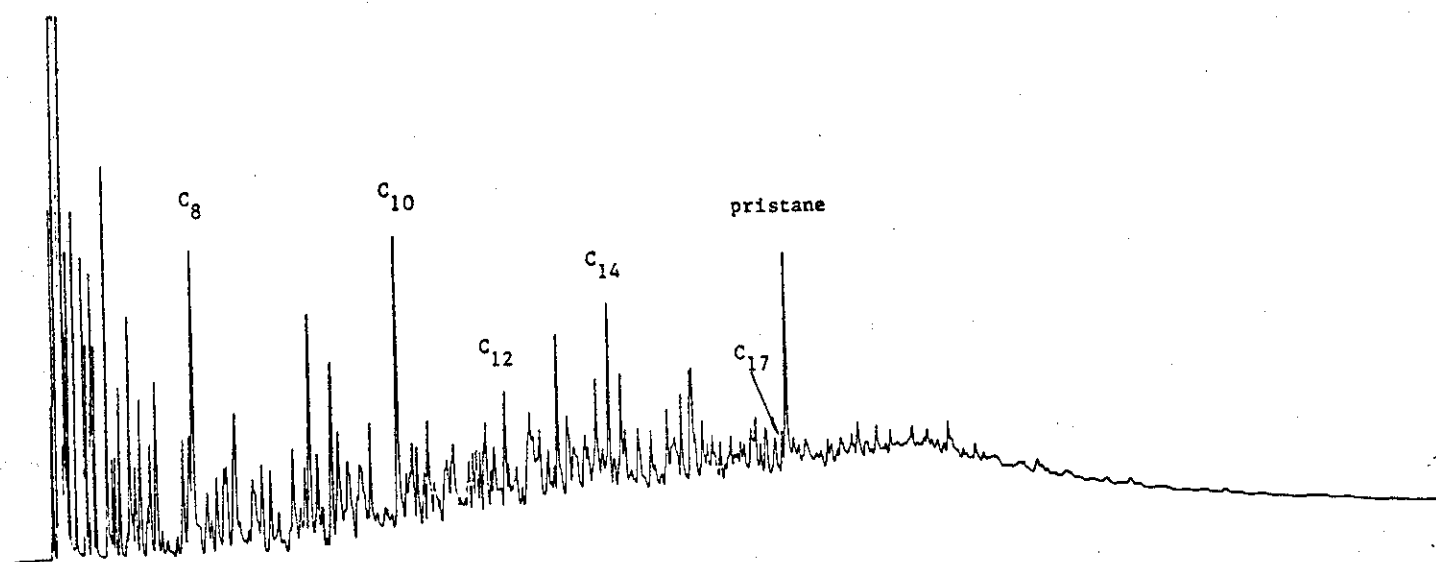


Figure 2.2 Gas chromatogram of fresh California Crude Oil API 11.

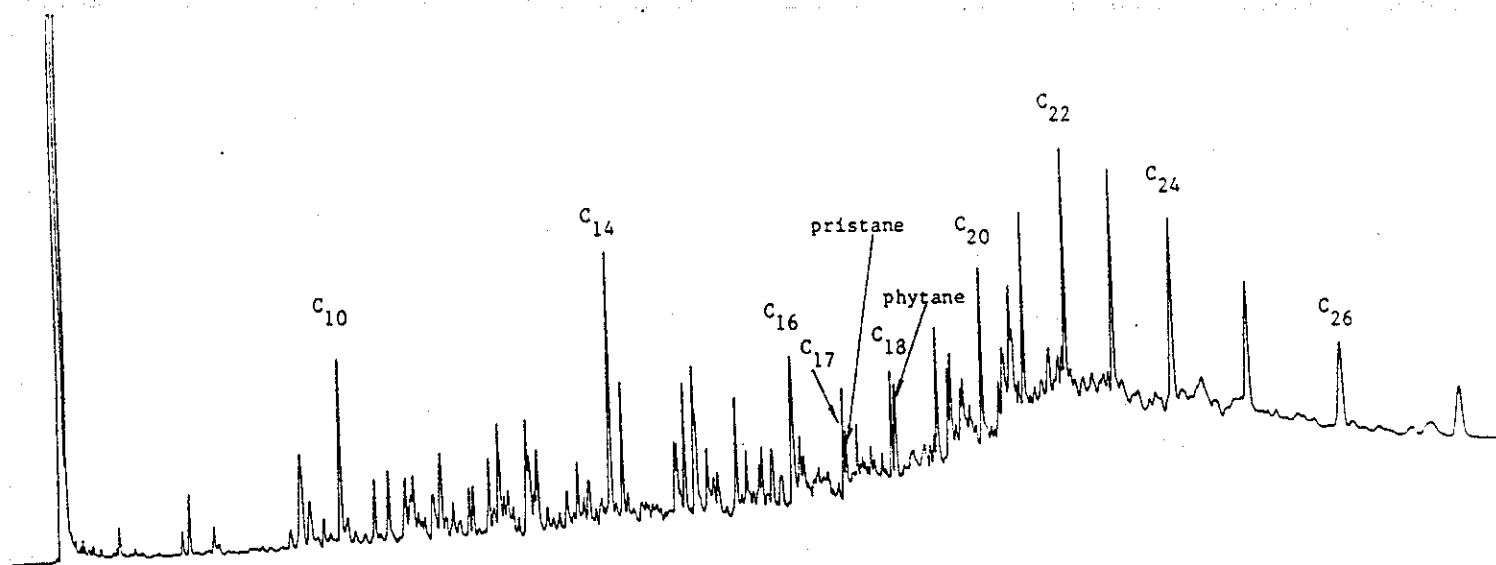


Figure 2.3 Gas chromatogram of fresh Bunker C Fuel Oil.

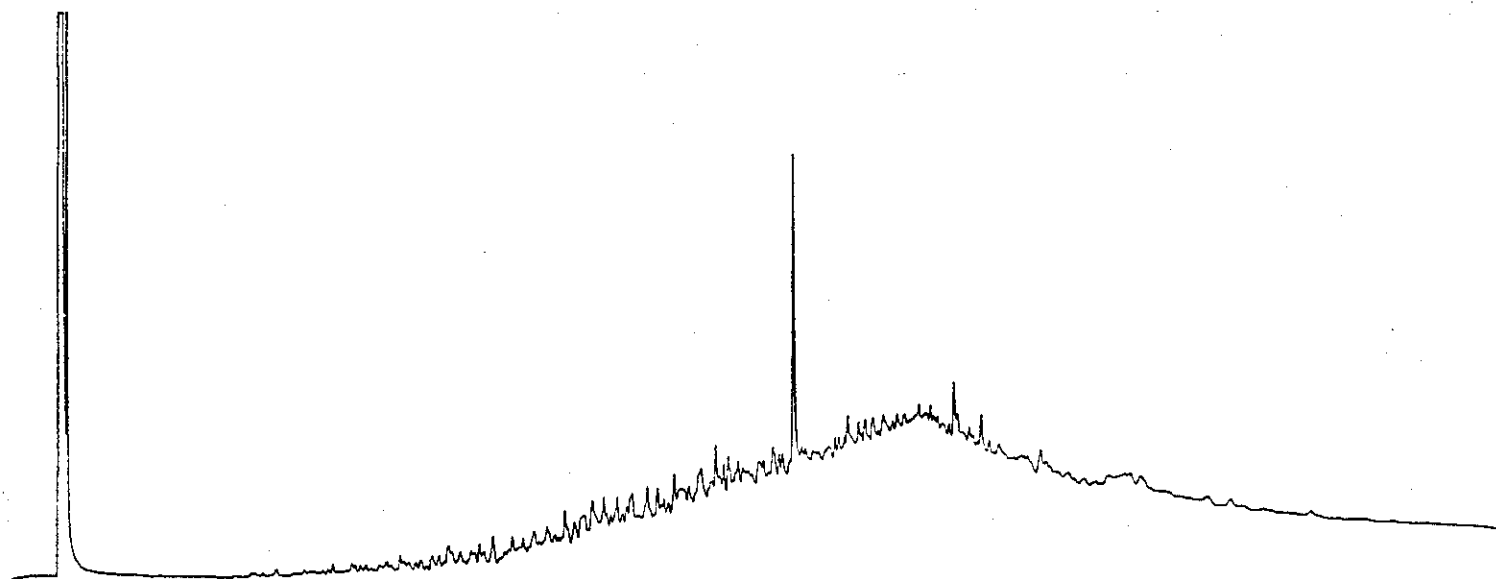


Figure 2.4 Gas chromatogram of fresh Cold Lake Bitumen.

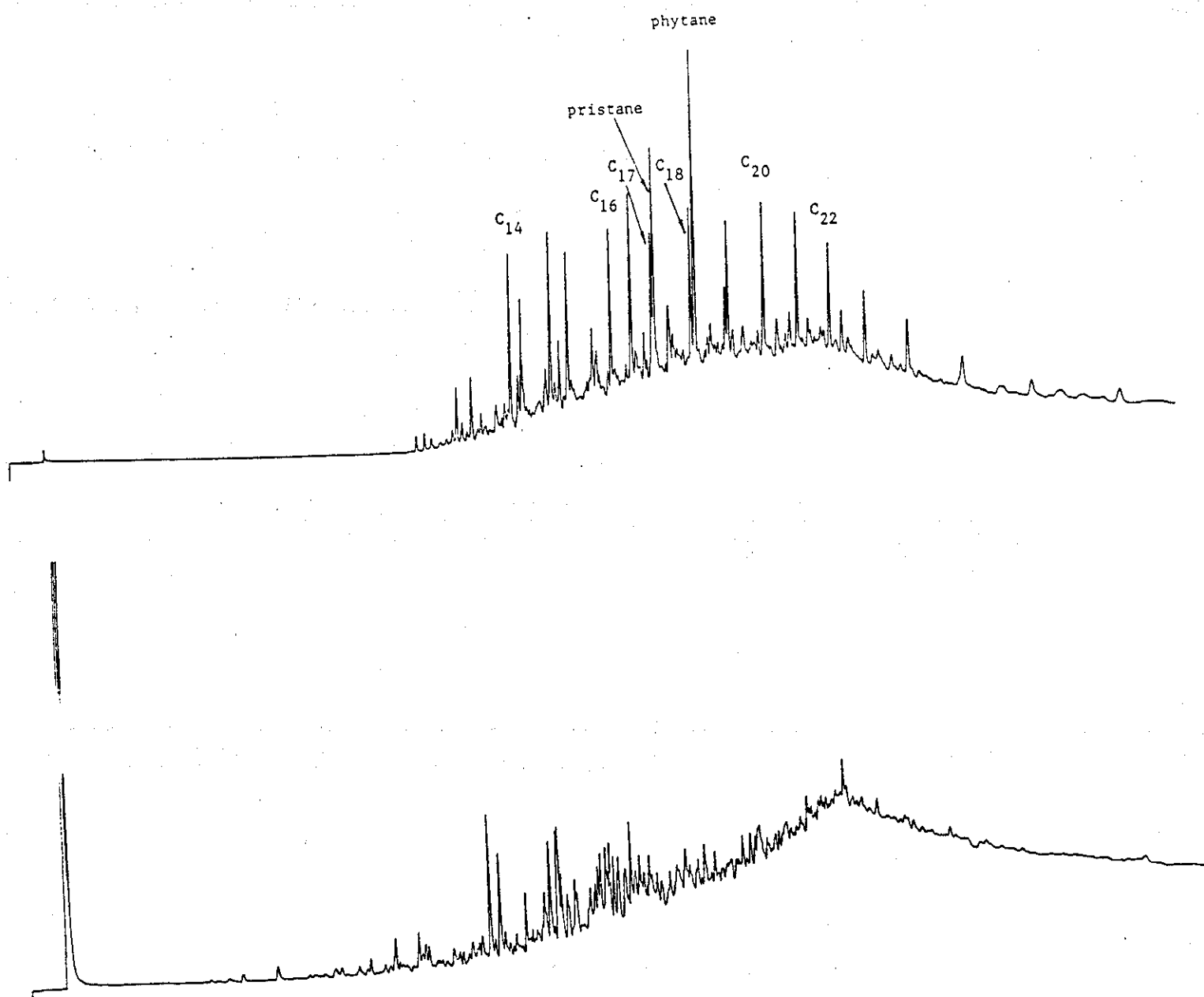


Figure 2.5 Gas chromatograms of saturate (above) and aromatic (below) fractions of California Crude Oil API 15.

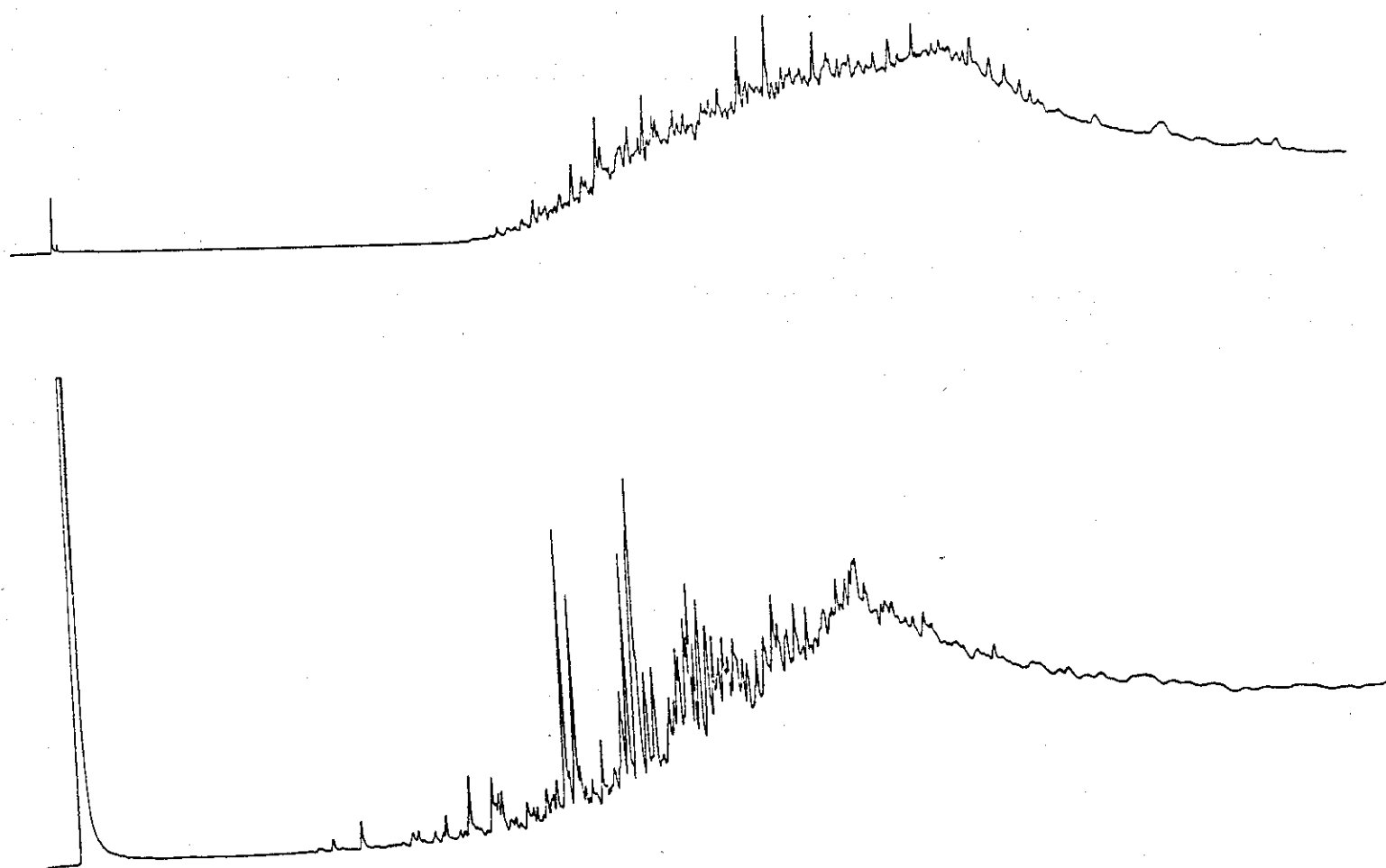


Figure 2.6 Gas chromatograms of saturate (above) and aromatic (below) fractions of California Crude Oil API 11.

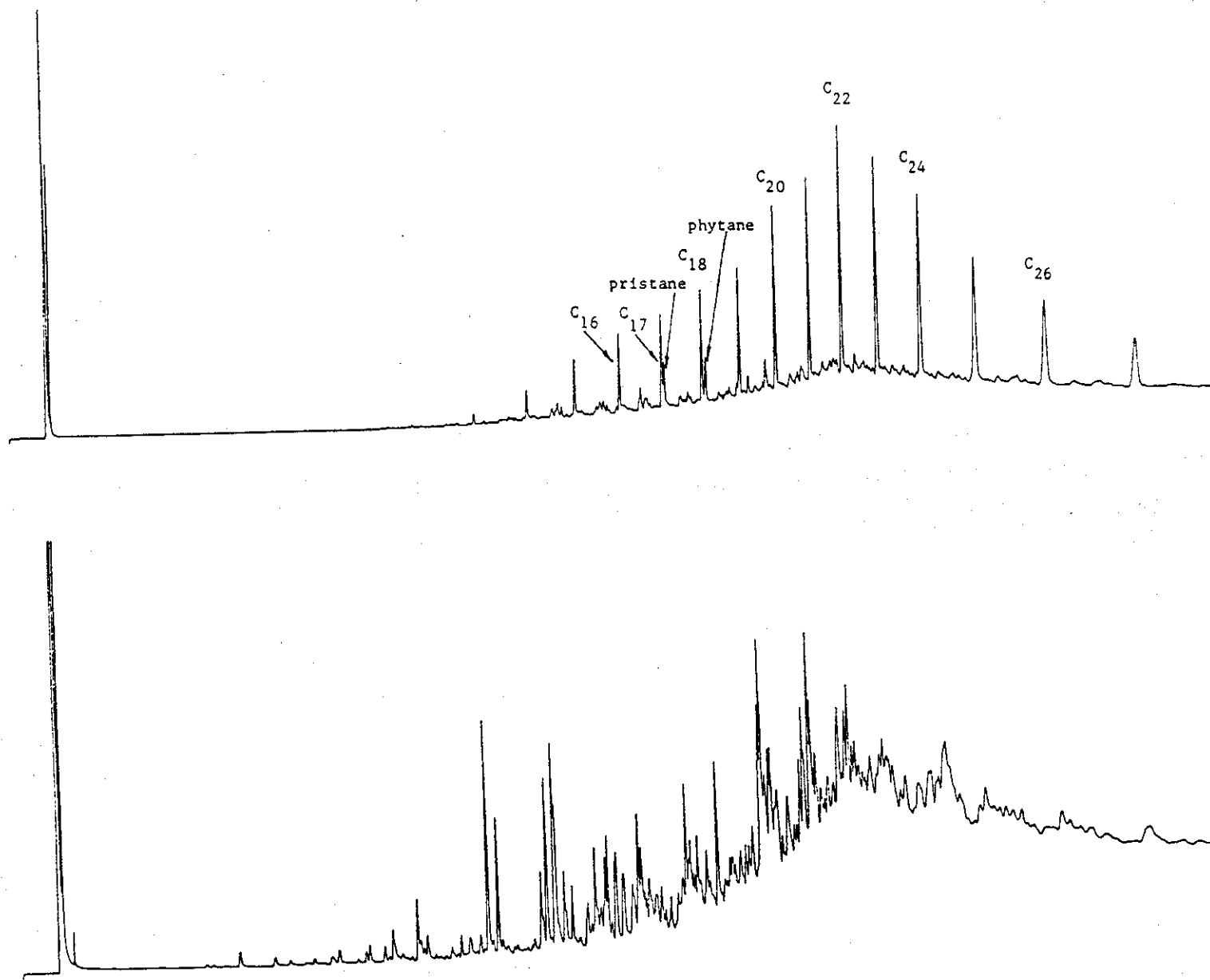


Figure 2.7 Gas chromatograms of saturate (above) and aromatic (below) fractions of Bunker C Fuel Oil.

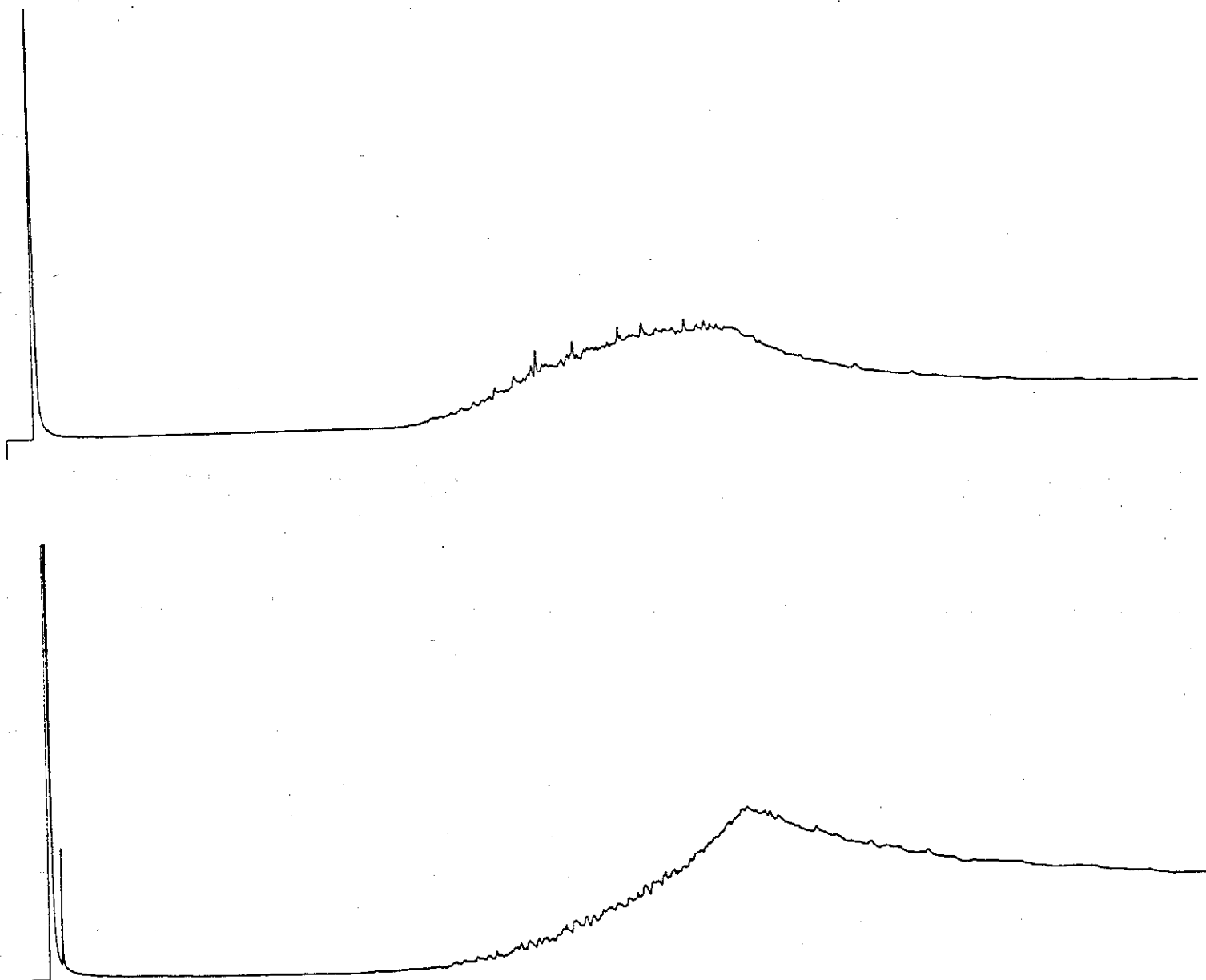


Figure 2.8 Gas chromatograms of saturate (above) and aromatic (below) fractions of Cold Lake Bitumen.

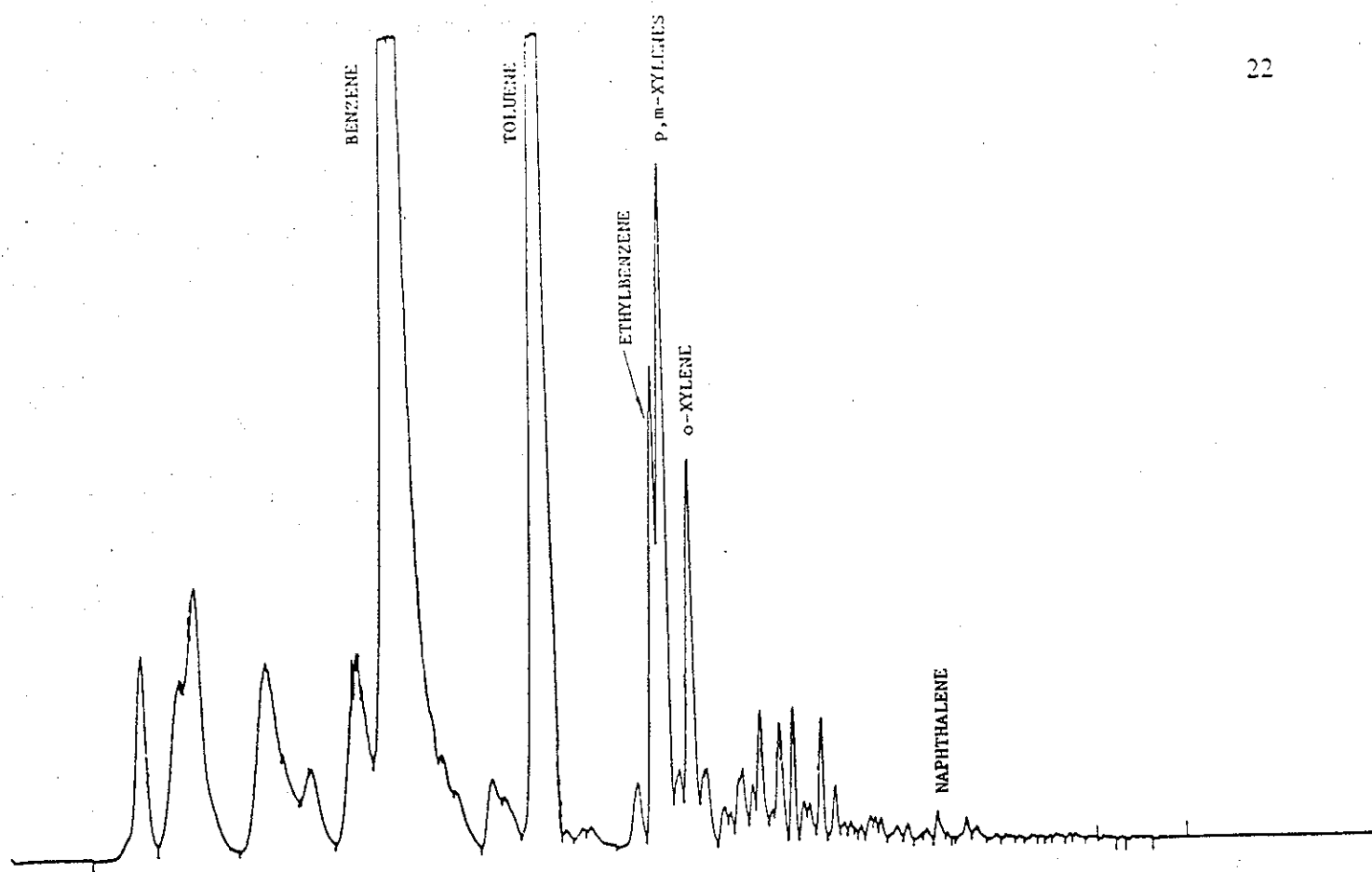


Figure 2.9 Gas chromatogram of WSF of California Crude Oil API 15.

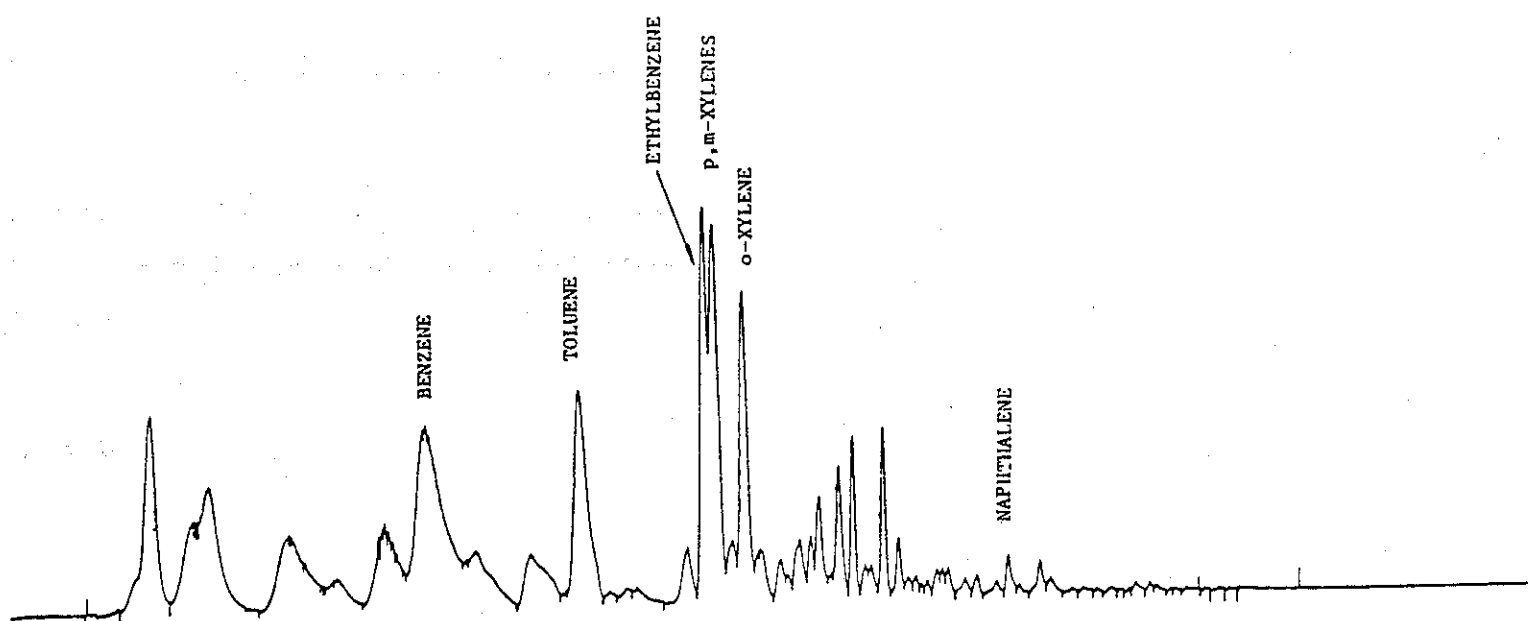


Figure 2.10 Gas chromatogram of WSF of California Crude Oil API 11.



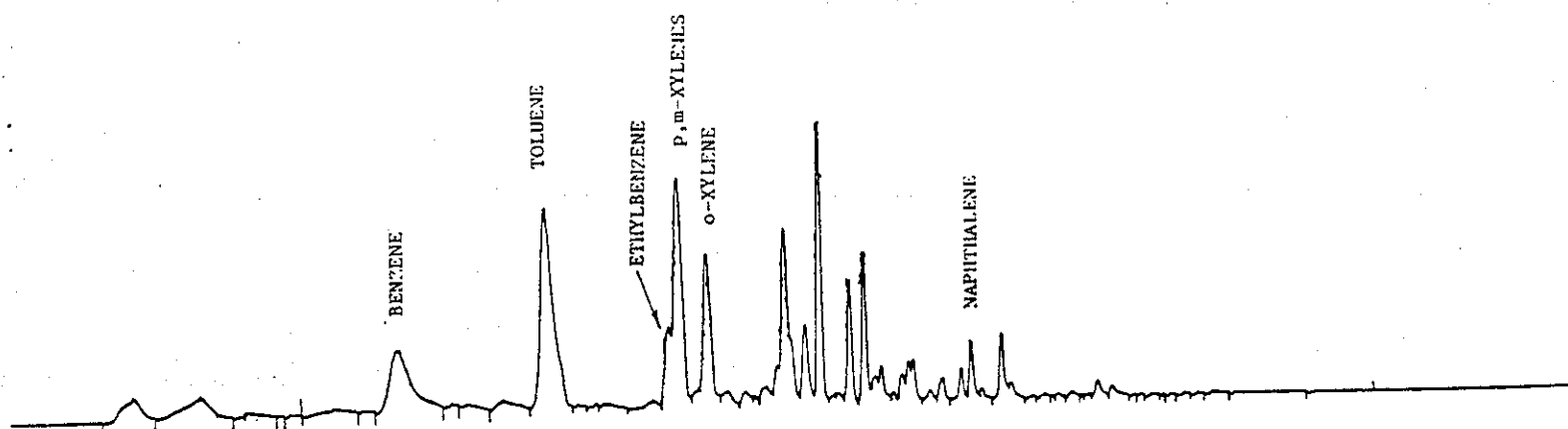


Figure 2.11 Gas chromatogram of WSF of Bunker C Fuel Oil.

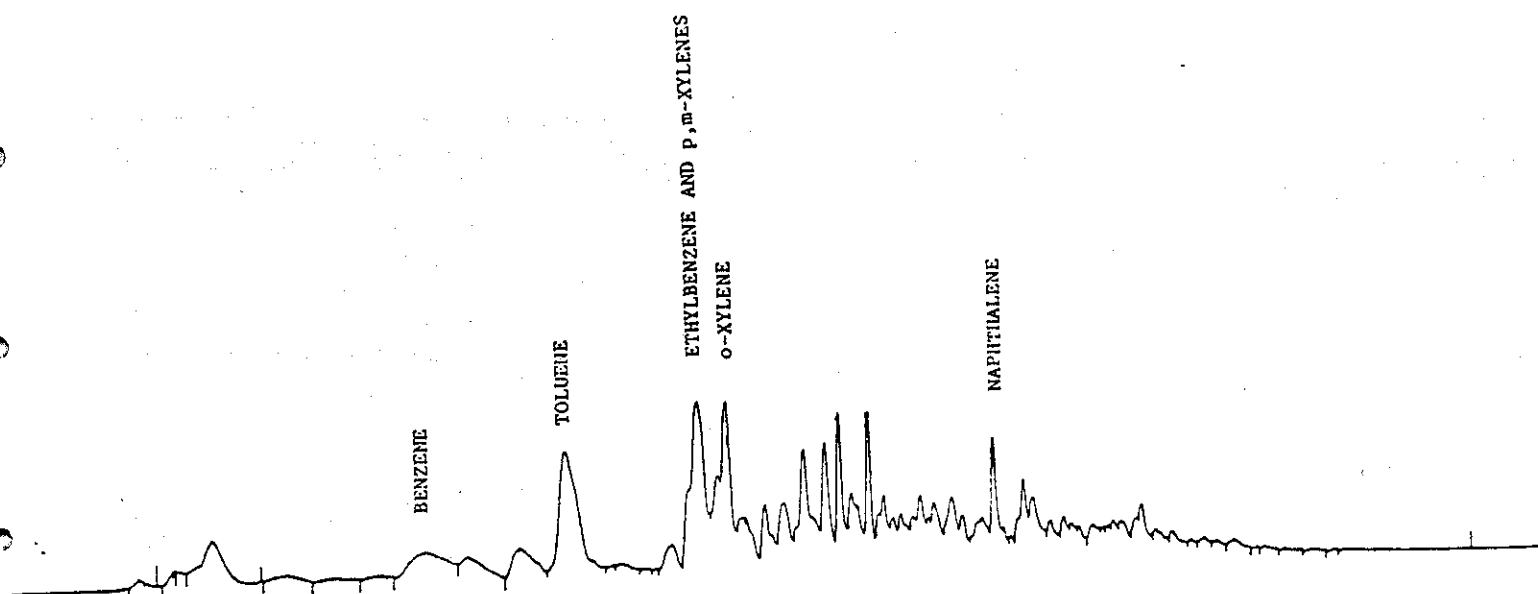


Figure 2.12 Gas chromatogram of WSF of Cold Lake Bitumen.

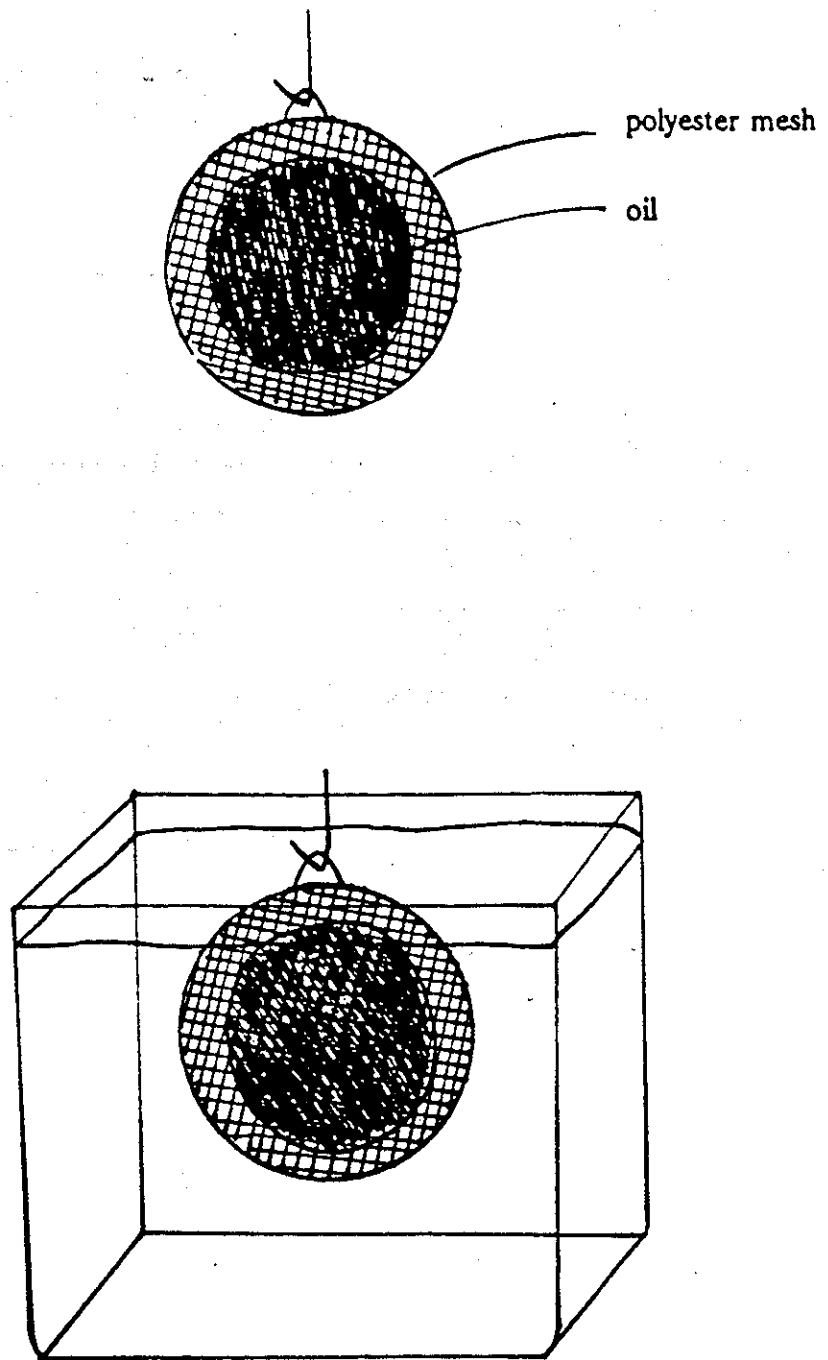


Figure 2.13 Diagram of experiment system in which oil-coated mesh disks are weighed in air and in water. The disk diameter is 6 cm.

### 3. MATHEMATICAL MODEL

#### 3.1 Introduction

The general aim of the mathematical model is to provide a quantitative description of the change in density of the oil as a function of exposures such as evaporation, dissolution, contact with solid materials and photolysis. This provides a method by which the experimental data may be converted into parameter values which can be used to correlate the data and possibly predict the effect of exposure to several density-increasing regimes. No previous models exist describing these density increases, thus the development described here is novel and undoubtedly will be the subject of improvement as a result of scrutiny and testing against future experimental data. The approach used should thus be regarded as exploratory in nature.

#### 3.2 Evaporation

In the interests of simplicity we first consider the oil to be a mixture of two components designated by subscripts 1 and R. Component 1 is subject to loss by evaporation while component R is inert or constitutes a residue which is unaffected by evaporation. It transpires that it is necessary to consider more than one evaporating component, however, this introduces little additional mathematical complexity, and it is preferable at this stage to treat only one evaporating component.

If we let the initial volumes be  $V_1$  and  $V_R$   $m^3$  and the densities  $D_1$  and  $D_R$   $kg/m^3$ , then the masses are  $M_1$  or  $V_1 D_1$  and  $M_R$  or  $V_R D_R$   $kg$ . The total volume is thus  $(V_1 + V_R)$ , the mass is  $(M_1 + M_R)$  and the mixture density is  $(M_1 + M_R)/(V_1 + V_R)$  or  $(V_1 D_1 + V_R D_R)/(V_1 + V_R)$  or  $y_1 D_1 + y_R D_R$ , where  $y_1$  is  $V_1/(V_1 + V_R)$  and  $y_R$  is  $V_R/(V_1 + V_R)$  and are the volume fractions of each component.

We postulate that component 1 is lost by evaporation at a rate proportional to its concentration, the area of exposure to evaporation ( $m^2$ ) and the mass transfer coefficient  $K$  ( $m/h$ ) namely

$$\text{Rate} = K A y_1 C_1^s \text{ mol/h}$$

In the evaporation process  $C_1^s$ , the concentration established by the evaporating component in the air phase (at the oil surface) is  $P_1^s/RT$  where  $P_1^s$  is the vapor pressure,  $R$  is the gas constant ( $8.314 \text{ Pa m}^3/\text{mol K}$ ) and  $T$  (K) is the absolute temperature. In units of mass loss in kilograms per hour the rate will be given by

$$\text{Rate} = K A y_1 C_1^s M_1 \text{ kg/h}$$

where  $M_1$  is the molecular mass of component 1 in units of kilogram per mole. The change in the amount of 1 will thus be given by

$$d(V_1 D_1)/dt = - K A y_1 C_1^s M_1$$

Now  $y_1$  is approximately  $V_1/V_R$  because  $V_R$  greatly exceeds  $V_1$ , thus

$$dV_1/V_1 = - (K A C_1^s M_1 / D_1 V_R) dt$$

which can be solved using an initial condition of  $V_1$  equal to  $V_{10}$  to give

$$V_1 = V_{10} \exp(- K A C_1^s M_1 t / D_1 V_R) = V_{10} \exp(- k_{E1} t)$$

where  $k_{E1}$  is  $K A C_1^s M_1 / D_1 V_R$  and is a rate constant for loss by evaporation.

Now  $V_R/A$  is approximately the oil thickness  $h$  and  $M_1/D_1$  is the molar volume  $v_1$  of the component and is expected to lie in the range  $200$  to  $500 \times 10^{-6} \text{ m}^3/\text{mol}$ . It follows that

$$k_{E1} = K C_1^s v_1 / h$$

The group  $C_1^s v_1$  is the saturation concentration of the component in the air in units of cubic metres of component per cubic metre of air. It is thus a saturation volume fraction in the air  $Y_1^s$ . Thus

$$k_{E1} = K Y_1^s / h$$

The characteristic time of reciprocal rate constant for this process is thus  $h/KY_1^s$  hours which can be read directly off a plot of the amount of component 1 or the density of the mixture as a function of time. The variation of density with time will thus be

$$D = (V_1 D_1 + V_R D_R) / (V_1 + V_R) = y_1 D_1 + (1 - y_1) D_R \\ = D_R - y_1 (D_R - D_1)$$

Substituting an exponential decrease in  $y_1$  similarly to that of  $V_1$  (since  $y_1$  is  $V_1/V_R$ ) and assuming that the volume of residue greatly exceeds the volume of the evaporating component we can assemble the equation for density as a function of time as shown below

$$D = D_R - y_{10} (D_R - D_1) \exp(-k_{E1}t)$$

where  $y_{10}$  is the initial volume fraction of component 1.

The density thus increases from an initial value of  $D_R - y_{10}(D_R - D_1)$  to  $D_R$  at infinite time. Experimentally we can measure both densities thus estimating  $y_{10}(D_R - D_1)$  and the time constant  $k_{E1}$ . In reality there are several components evaporating thus it may be necessary to include more components by expanding this expression to give an equation of the form below

$$D = D_R - y_{10}(D_R - D_1) \exp(-k_{E1}t) - y_{20}(D_R - D_2) \exp(-k_{E2}t)$$

In practice it is impossible to determine  $y_{10}$  and  $D_1$  separately, only the group  $y_{10}(D_R - D_1)$  can be estimated. This is because there is no experimental method of discriminating between dissolution of a small amount of material of low density and a larger amount of material of higher density. In the interests of algebraic simplicity the group  $y_{10}(D_R - D_1)$  is designated as  $E_1$ , and the group for the second evaporation component as  $E_2$  giving the simpler overall equation

$$D = D_R - E_1 \exp(-k_{E1}t) - E_2 \exp(-k_{E2}t)$$

This can be rearranged to give an expression for the density increase from that of the fresh oil density, i.e.  $(D_R - E_1 - E_2)$  namely

$$\Delta D_E = E_1(1 - \exp(-k_{E1}t)) + E_2(1 - \exp(-k_{E2}t))$$

Further, rather than report  $k_{E1}$  and  $k_{E2}$  as reciprocal times (e.g.  $0.01 \text{ h}^{-1}$ ) it is more meaningful to report them as  $1/T_{E1}$  and  $1/T_{E2}$  where  $T_{E1}$  and  $T_{E2}$  are characteristic times, e.g. 100 hours.

### 3.3 Dissolution

A similar analysis can be conducted for dissolution invoking a dissolution mass transfer coefficient. In this case the equation is identical but the concentration  $C_1^s$  becomes the solubility of component 1 in water rather than the solubility in air. The mass transfer coefficient will of course be different for dissolution from that for evaporation. Using the same mathematical procedure results in an equation for density increase as a function of dissolution which is identical in structure to that for evaporation, except that for reasons discussed later only one term is justified.

$$D = D_R - F_1 \exp(-k_{D1}t)$$

or

$$\Delta D_D = F_1(1 - \exp(-k_{D1}t))$$

### 3.4 Simultaneous Evaporation and Dissolution

If the components which evaporate are not those which dissolve then the equations for evaporation and dissolution could be essentially added and evaporating and dissolving components could be identified separately. In reality this is unlikely to apply because the components which dissolve will tend to be those of lower molecular weight which probably are also subject to evaporation, i.e.  $E_1$  and  $F_1$  are equivalent. It is therefore probably more reliable to add the rate constants for evaporation and dissolution and apply them to the same component thus giving an equation of the form shown below for two components

$$D = D_R - E_1 \exp(-(k_{E1} + k_{D1})t) - E_2 \exp(-k_{E2}t)$$

or

$$\Delta D_{DE} = E_1(1 - \exp(-(k_{E1} + k_{D1})t)) + E_2(1 - \exp(-k_{E2}t))$$

### 3.5 Photolysis

For photolysis we postulate a similar relationship of the form.

$$\Delta D_P = G(1 - \exp(-k_P t))$$

where  $G$  is the final density increase caused by photolytic processes. Some justification for this approach is obtained by noting that photolysis occurs to a limited fraction of the oil, namely that at the oil surface.

### 3.6 Attachment of Foreign Matter

When foreign matter such as clay, microorganisms or diatomaceous matter becomes attached to the oil the bulk density of the oil will increase according to the equation

$$D = ZD_F + (1 - Z)D_o$$

where  $Z$  is the volume fraction of foreign matter of density  $D_F$  and  $D_o$  is the oil density. This can be rearranged to the more convenient form below expressing density as a function of the difference between the solid density and the oil density. If it is desired to express  $Z$  as a function of time then a suitable expression would be simply a first order increase as given below

$$\begin{aligned} D &= D_o + Z(D_F - D_o) \\ \Delta D_F &= D - D_o = Z(D_F - D_o) \\ Z &= Z_F(1 - \exp(-k_F t)) \end{aligned}$$

where  $Z_F$  is the final value of  $Z$  and  $k_F$  is a rate constant.

As is discussed later there appears to be a non linear density increase with an initial rapid uptake followed by a slower uptake. This may be due to a viscosity increase or the coverage of the surface by mineral matter.

### 3.7 Overall Density Equation

Combining the expressions for evaporation dissolution, photolysis and attachment of foreign matter, the density of an oil mass is postulated to be described by the equation given below which contains adjustable parameters for the various processes. Examination of the magnitude of the parameters will show which of the processes are important and the rates of the density increase which can be expected

$$D = D_o + \Delta D_{DE} + \Delta D_F + \Delta D_F$$

The key problem is to obtain values of the parameters  $E_1$  (or  $F_1$ ),  $E_2$ ,  $G$ ,  $Z_F$ ,  $D_F$  and the various rate constants then determine how fast the density  $D$  increases and if, in doing so, how it will approach and eventually exceed that of seawater.

### 3.8 A Theoretical Exploration of the Relative Roles of Evaporation and Dissolution

In this section we speculate on the likely relative importance of evaporation and dissolution processes as methods by which oil components migrate from the oil mass causing a density increase. As was discussed earlier the rates of these processes can be expressed as

$$N = K A y_i C_i^s \text{ mol/h}$$

where  $K$  is an evaporation or dissolution mass transfer coefficient,  $A$  is the evaporation area (i.e. oil area exposed to air) or the dissolution area (i.e. oil exposed to water),  $y_i$  is the mole fraction of the chemical of interest and  $C_i^s$  is the saturated air concentration (for evaporation) or the saturated water concentration (solubility) for dissolution. The ratio of evaporation to dissolution rates can then be expressed as  $R_{ED}$

$$R_{ED} = N_E/N_D = (K_E/K_D)(A_E/A_D)(C_E^s/C_D^s)$$

The ratio of mass transfer coefficients can be estimated from reported values, albeit with considerable uncertainty. A typical  $K_E$  is 1000 to 5000 cm/h, whereas  $K_D$  is constrained to a much lower range of 2 to 20 cm/h by virtue of the lower diffusivity in water. Their ratio is thus typically 500 to 250, with 400 being a reasonable value. This is the same order of magnitude as the square root of air and water diffusivities, in accordance with penetration theory.

The exposed area ratio will range from about 1.0 for a floating oil mass to perhaps 0.01 or less for an overwashed mass. It is possible that overwashed oil has a continuous water film, thus the ratio could be effectively zero.



Finally  $C_E^s/C_D^s$  is the air/water partition coefficient of the hydrocarbon. Some values taken from Mackay and Shiu (1981) are given below in Table 3.1. The Henry's Law Constant  $H$  has units of  $\text{kPa m}^3/\text{mol}$ , from which the air/water partition coefficient  $K_{Aw}$  is deduced as

$$K_{Aw} = H \times 1000/R.T = H \times 1000/8.314 \times 298 = 0.4 H$$

Table 3.1 Partitioning Characteristics of Selected Hydrocarbons

Hydrocarbon	H	$K_{Aw}$	$R_{ED}$ for Area Ratios		
			1.0	0.1	0.01
octane	300	120	40000	4000	400
dodecane	700	280			
tetradecane	100	40			
benzene	0.55	0.22	40	4	0.4
p-xylene	0.71	0.28			
n-butylbenzene	0.13	0.05			
naphthalene	0.043	0.017	1.2	0.12	0.012
fluorene	0.008	0.003			
anthracene	0.006	0.002			
pyrene	0.001	0.0004			

It is apparent that alkanes have  $K_{Aw}$  values of 40 to 280 with 100 being a typical value, whereas the more soluble aromatics range from 0.05 to 0.3 with 0.1 being typical. The PAHs are generally about 0.001 to 0.01, 0.003 being typical.

For interest we can calculate  $R_{ED}$  for these classes for  $(K_E/K_D)$  of 400 and area ratios of 1, 0.1 and 0.01. This is done in Table 3.1.

Clearly the alkanes are primarily lost by evaporation. The small amount of alkane which may dissolve will rapidly evaporate from solution. It can be argued that it will be almost impossible to detect alkane dissolution in a system in which the oil is exposed to air even for one fraction of a percent of the exposure time. The mono-aromatics will predominantly evaporate, but they may be

lost by dissolution if appreciably submerged, but again even a little evaporation may obscure the effect of dissolution. Finally it is likely that the PAHs will be lost mainly by dissolution.

Also of interest is the absolute rates of these processes, i.e.  $N_E$  and  $N_D$ . For unit area the rates are

$$N_E = K_E C_E^S \text{ or } K_E P^S / RT$$

$P^S$  is vapor pressure (Pa)

$$N_D = K_D C_D^S \text{ or } K_D S^S / M$$

$S^S$  is solubility ( $\text{g}/\text{m}^3$ ) and  $M$  is molecular mass

Adapting illustrative values of 30.00 for  $K_E$  and 0.075 (m/h) for  $K_D$  (ratio 400), then for dodecane ( $P^S = 16$ ,  $S^S = 0.003$ ,  $M = 170$ )

$$N_E = 0.19$$

$$N_D = 1.3 \times 10^{-6}$$

both  $\text{mol}/\text{m}^2\cdot\text{h}$

For anthracene ( $P^S = 1.4 \times 10^{-3}$  Pa,  $S = 0.05$ ,  $M = 178$ )

$$N_E = 1.7 \times 10^{-5}$$

$$N_D = 2.1 \times 10^{-5}$$

$\text{mol}/\text{m}^2\cdot\text{h}$

An oil film  $1 \text{ m}^2$  in area and 1 mm thick has a volume of  $10^{-3} \text{ m}^3$  or 1 litre and probably contains 5 mol of hydrocarbon in total. Losses of 0.05 mol (1%) are significant, which will require 2500 h at a rate of  $2 \times 10^{-5} \text{ mol}/\text{m}^2\cdot\text{h}$ , i.e. about 100 days. It is thus apparent that for weathering to be significant, e.g. 1% in 100 hours, requires a rate of  $5 \times 10^{-4} \text{ mol}/\text{m}^2\cdot\text{h}$  which in turn requires a vapor pressure of the order of 0.04 Pa (the approximate vapor pressure of hexadecane) or a solubility of  $1.3 \text{ g}/\text{m}^3$  (approximately that of phenanthrene).

Hydrocarbons which have vapor pressures below  $10^{-2}$  Pa or solubilities below  $1 \text{ g}/\text{m}^3$  will be substantially retained by the oil and are unable to migrate into air or water because of the very low concentrations which they can establish in these phases.

The alkanes to about  $C_{16}$ , the monoaromatics, the naphthalenes, the three membered PAHs and polar "hydrocarbons" containing O, N or S atoms are thus candidates for loss by evaporation or dissolution. The others are probably destined to remain in the oil. A consequence of this analysis is that it may often be fruitless to look in the oil phase for evidence of loss of these chemicals, rather they should be sought in the "receiving" phases of air or water, i.e. the water solubility or

partial pressure of these chemicals should be measured as indicators of potential for migration from oil and thus for causing density increases.

### 3.9 The Role of Submergence

It should be recognised that the condition of the oil on the sea surface will influence the density increase. For example, dense oil masses will tend to be appreciably submerged and thus shielded from evaporation. Solar radiation will vary with latitude, time of year and cloud cover. Thin oil slicks with higher area to volume ratios will be subject to more rapid weathering. It follows that 1 day's exposure to evaporation in the laboratory will not necessarily be equivalent to one day at the ocean surface, i.e. the "exposure" regimes will be different.

The primary thrust of this study is to measure and correlate density increases in the laboratory under defined conditions. A second and separate task is to relate these exposure regimes. This issue is discussed later in this report in more detail.

## 4. RESULTS

### 4.1 Evaporation

The first series of evaporation tests lasted for 21 days and showed that the oil density was increasing with time and served to confirm that the experimental method was valid. As a result of experience in this series, the number of replicates was increased from 3 to 5 and additional measurements of oil density were made early during the evaporation period because there was clearly a rapid increase in oil density during the first day. The second series of evaporation experiments yielded improved accuracy and a smaller standard deviation. The individual results for the four oils during this series are given in Figures 4.1 to 4.4 and for comparative purposes are combined in Figure 4.5. All oils showed a density increase during the first day presumably because of loss of volatile material. The Bunker C oil showed a relatively small increase presumably as a result of loss of volatile material during distillation. The Cold Lake bitumen also showed a fairly small increase in density. The two crude oils showed larger density increases and there was a continual increase in density after three or four days.

The magnitude of the density increase is significant and would have a major effect on the oil's submergence and sinking behaviour.

Examination of the curves suggest that accurate description of density increase require the incorporation of at least three components in the system, i.e. two components which evaporate and a residue. The first component appears to evaporate with a time constant of the order of two days or 50 hours and the second one with a time constant of approximately 16 days or 400 hours. The two crude oils, C11 and C15, eventually display densities approaching that of sea water.

Fitting these data to the evaporation equation presented earlier gives the following approximate parameter values. The lines corresponding to these parameter values are plotted on the Figures.

Table 4.1 Evaporation Parameters

<u>Oil</u>	<u>E, kg/m<sup>3</sup></u>	<u>k, h<sup>-1</sup></u>	<u>E, kg/m<sup>3</sup></u>	<u>k, h<sup>-1</sup></u>
C11	38	1/20	15	1/400
C15	51	1/20	13	1/400
CLB	17	1/20	13	1/400
BC	16	1/20	3	1/400

A note of caution is appropriate to the interpretation of these results. The experimental technique is believed to be valid as a means of detecting density increases. The technique suffers from appreciable error in determining absolute densities because of the errors introduced in weighing and subtracting mesh masses and volumes. Occasionally a small amount of oil would float from the mesh surface thus confounding the density determination. It is possible that water dissolved in the oil thus affecting its weight in air, but not its weight in water. A compromise had to be made between prolonged drying with excessive evaporation and short drying with risk of retained water. Emphasis should be placed on the trends in relative density, not on absolute density.

#### 4.2 Evaporation Plus Photolysis

The effect of photolysis is shown in Figures 4.6 to 4.9 with the evaporation results also included as points and a line for comparison. In most cases, the exception being oil C11, the photolyzed oil shows increases in density beyond that of the evaporated oils suggesting that photolysis either enhances evaporation (possibly by increasing the surface temperature of the oil) or results in formation of denser oil species. It was of course impossible to study photolysis in air in the absence of evaporation thus the approach taken was to calculate the increase in density of the photolyzed oil attributable to photolysis beyond that which occurred for the second evaporation experiment and attribute that incremental increase in density to photolytic process. For example, for CLB and BC that increase corresponds to a density increment of about 5 kg/m<sup>3</sup> at 14 days or 336 hours. For C11 and C15 oils, the increase in densities attributable to photolysis was judged to be within the range of experimental error and no definite conclusion can be reached that photolysis causes an additional increase in oil density.

Fitting these data to the model suggests that the values in Table 4.2 can be used.

Table 4.2 Photolysis Parameters

<u>Oil</u>	<u>G (h<sup>-1</sup>)</u>	<u>k<sub>p</sub> h<sup>-1</sup></u>
C11	0	1/400
C15	0	1/400
CLB	12	1/400
BC	2	1/400

#### 4.3 Dissolution

Experiments were run in parallel using fresh deionized distilled water and using salt water. The oil was not exposed to light except during the density measurements and the water was changed periodically to remove any components which had dissolved. The experiments ran for 42 days and showed a small increase in density as shown in Figures 4.10 and 4.11. The variation in density was more erratic during these dissolution experiments. This is partly due to some difficulties experienced experimentally in which there may have been loss of some of the oil from the meshes during the exposure. It appears that the crude oils show a more significant increase in density probably as a result of the presence of more soluble lower molecular weight material. The density increase is in the range 24 to 31 kg/m<sup>3</sup> for the crude oils and is about 15 kg/m<sup>3</sup> for the fuel oils.

Fitting a one-dissolving component model gives the parameters below.

Table 4.3 Dissolution Parameters

<u>Oil</u>	<u>Fresh Water</u>		<u>Salt Water</u>	
	<u>F<sub>i</sub> kg/m<sup>3</sup></u>	<u>k<sub>Di</sub> h<sup>-1</sup></u>	<u>F<sub>i</sub> kg/m<sup>3</sup></u>	<u>k<sub>Di</sub> h<sup>-1</sup></u>
C11	38	1/1000	42	1/400
C15	51	1/1000	68	1/400
CLB	17	1/1000	19	1/400
BC	16	1/1000	17	1/400

Part of this density increase may be due to evaporation. Support for this comes from the relative magnitudes of the  $E_1$  parameters in Table 4.1 and the  $F_1$  parameters in Table 4.3. Seven measurements of density involved exposing the oil to approximately 20 hours of evaporation, thus the observation that the  $F_1$  values are some 75% of the  $E_1$  values suggests that some evaporation may have occurred, but the rate is much slower, i.e. by a factor of ten.

The most notable feature of the dissolution effect is its slowness (i.e. low  $k_1$ ) relative to evaporation.

The salt water results in Figure 4.11 show a greater increase in density especially for the crude oils. This was not expected and the reasons for it are unknown. It seems unlikely, but it is not impossible, that the oil picks up salt possibly through the formation of sodium salts of carboxylic and phenolic acids.

#### 4.4 Additional Photolysis Experiments

Two additional photolysis experiments were run, one in air, in which evaporation is inevitably present, and one in stagnant water. The results confirmed that the increase in density attributable to photolysis can be significant. The results in water were quite variable. It was observed that the colour of the oil surface changed after about two weeks probably as a result of free radical initiated reactions forming a polymeric substance. The results are given in Figures 4.12 and 4.13.

#### 4.5 Attachment of Suspended Matter

Two series of experiments were taken investigating the attachment of suspended solid matter to the oils. The initial results for clay demonstrated a density increase of the order of  $80 \text{ kg/m}^3$ . The tests using C15 oil in the presence of microorganisms showed a much smaller increase of the order  $30 \text{ kg/m}^3$  but with very highly variable. The second series of experiments yielded more accurate data and are discussed in more detail.

Figure 4.14 to 4.18 give the density increases for the various mineral materials. When compiling these data the corresponding density increase attributable to dissolution has not been subtracted to give only the estimated increase due to attachment of solids. In these tests the densities increased considerably, i.e. by 60 to  $70 \text{ kg/m}^3$  often reaching a value higher than that of seawater.

There did not appear to be any strong influence of mineral type. The principal differences in behaviour between mineral types is attributable to differences in suspended solids contents. Some minerals (notably talc) proved to be difficult to maintain in suspension. Various approaches were tested in an attempt to standardize the solids concentration but this proved to be a formidable experimental task. It is estimated that the suspended matter concentration in these tests ranged from 50 to 250 mg/L.

Fitting the model to these data gave the following parameter values:

Table 4.4 Foreign Matter Attachment Parameters

	C15		CLB	
	$Z_r$	$K_r (h^{-1})$	$Z_r$	$K_r (h^{-1})$
Pottery Clay	0.032	1/50	0.042	1/75
Talc	0.023	1/50	0.03	1/75
River Clay	0.02	1/50	0.022	1/75
Kaolinite	0.016	1/50	0.02	1/75
Diatomaceous Earth	0.022	1/50	0.026	1/75

It is satisfying that the  $Z_r$  values are fairly constant suggesting that for an oil mass of this area/volume ratio exposed to a suspension for some 200 hours, the oil will pick up about 4% of its volume of foreign matter.

Some of this density increase may be due to dissolution, but the magnitude is believed to be small. Evaporation was avoided by leaving the samples submerged at all times.



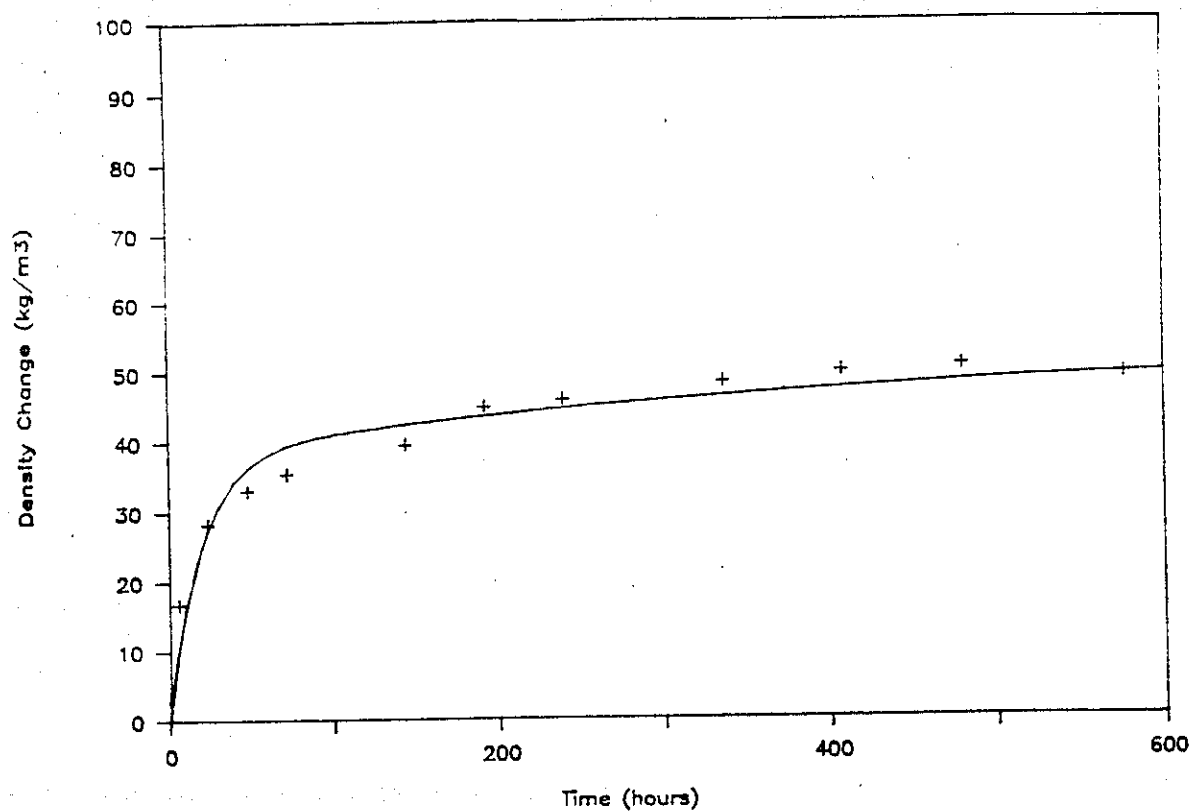


Figure 4.1 Evaporation of California Crude Oil API 11.

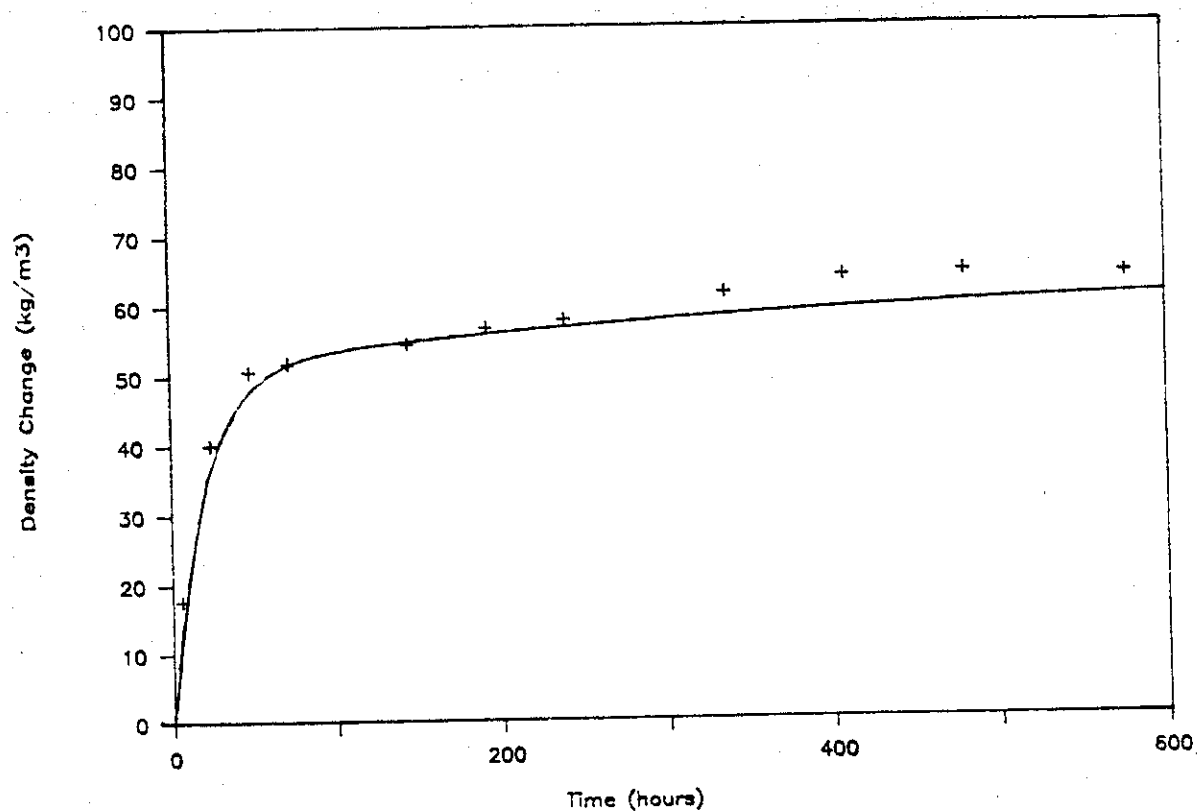


Figure 4.2 Evaporation of California Crude Oil API 15.

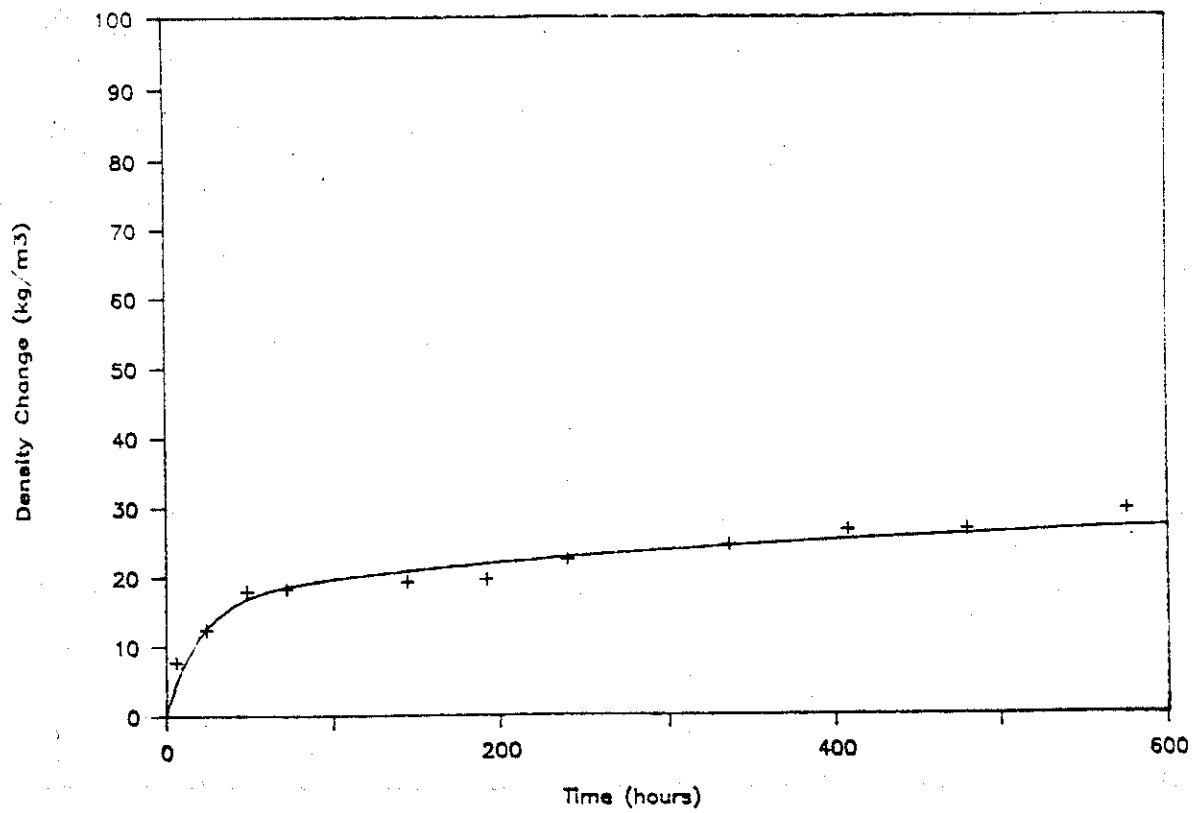


Figure 4.3 Evaporation of Cold Lake Bitumen.

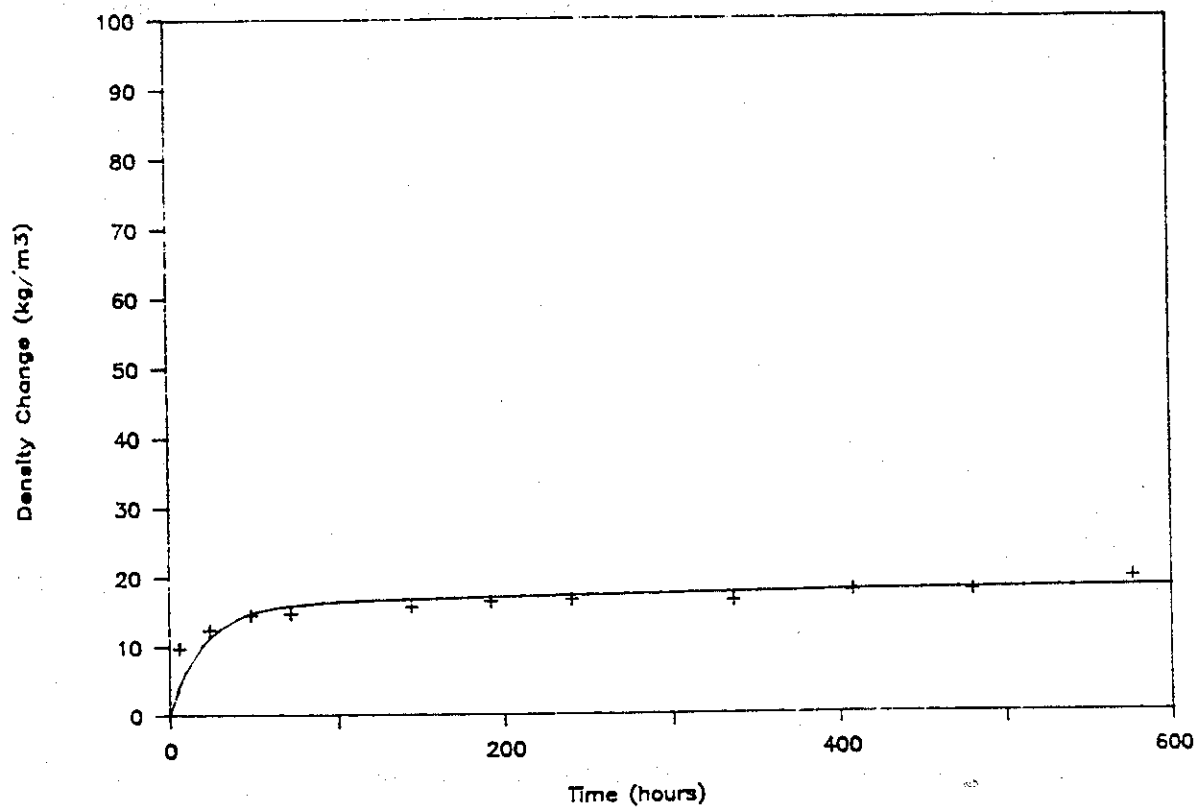


Figure 4.4 Evaporation of Bunker C Fuel Oil.

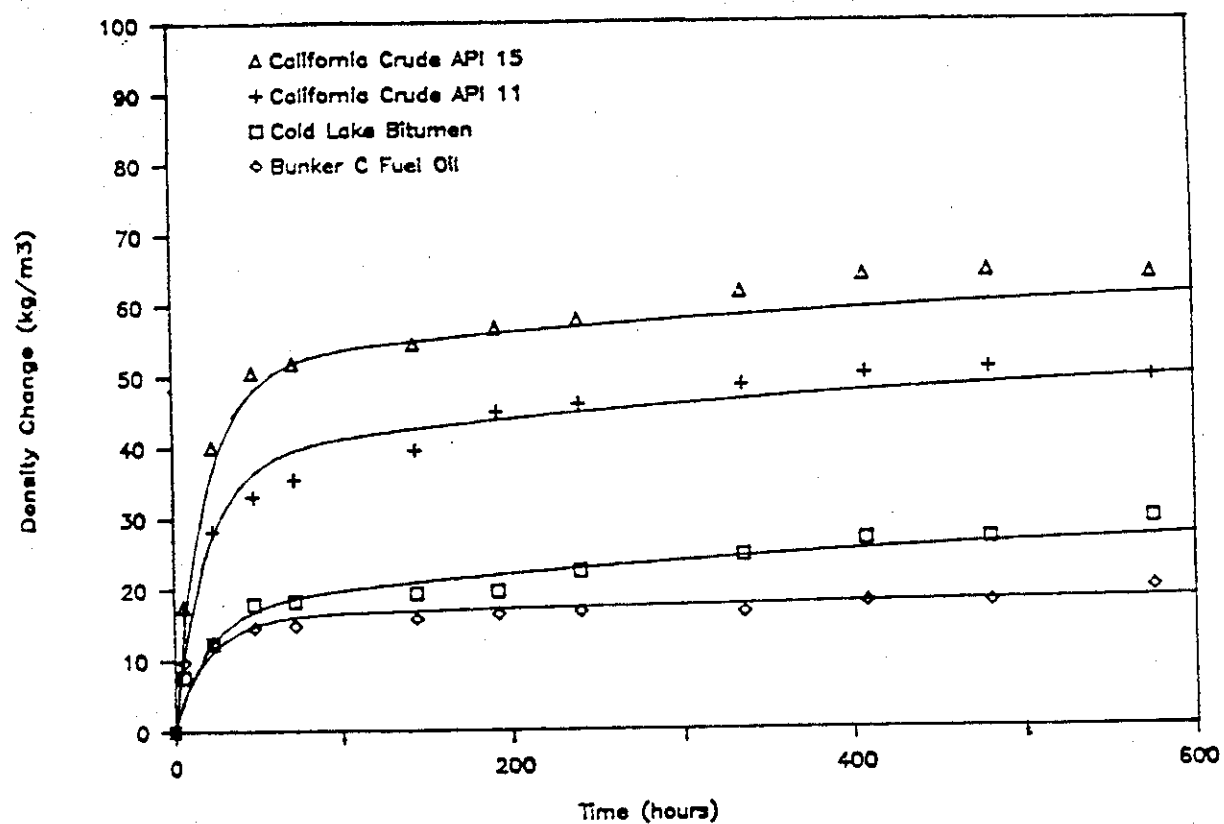


Figure 4.5 Evaporation of crude oils and residual fuels.

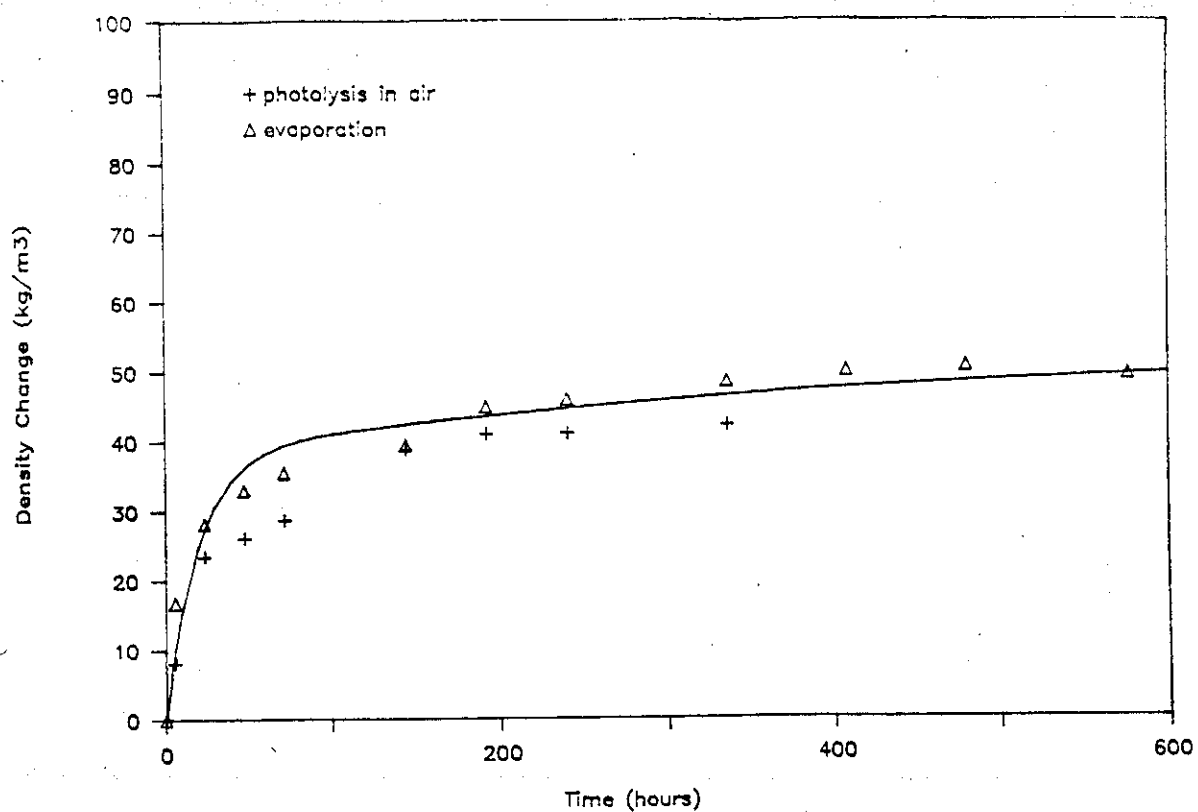


Figure 4.6 Effect of California Crude Oil API 11 exposed to photolysis.

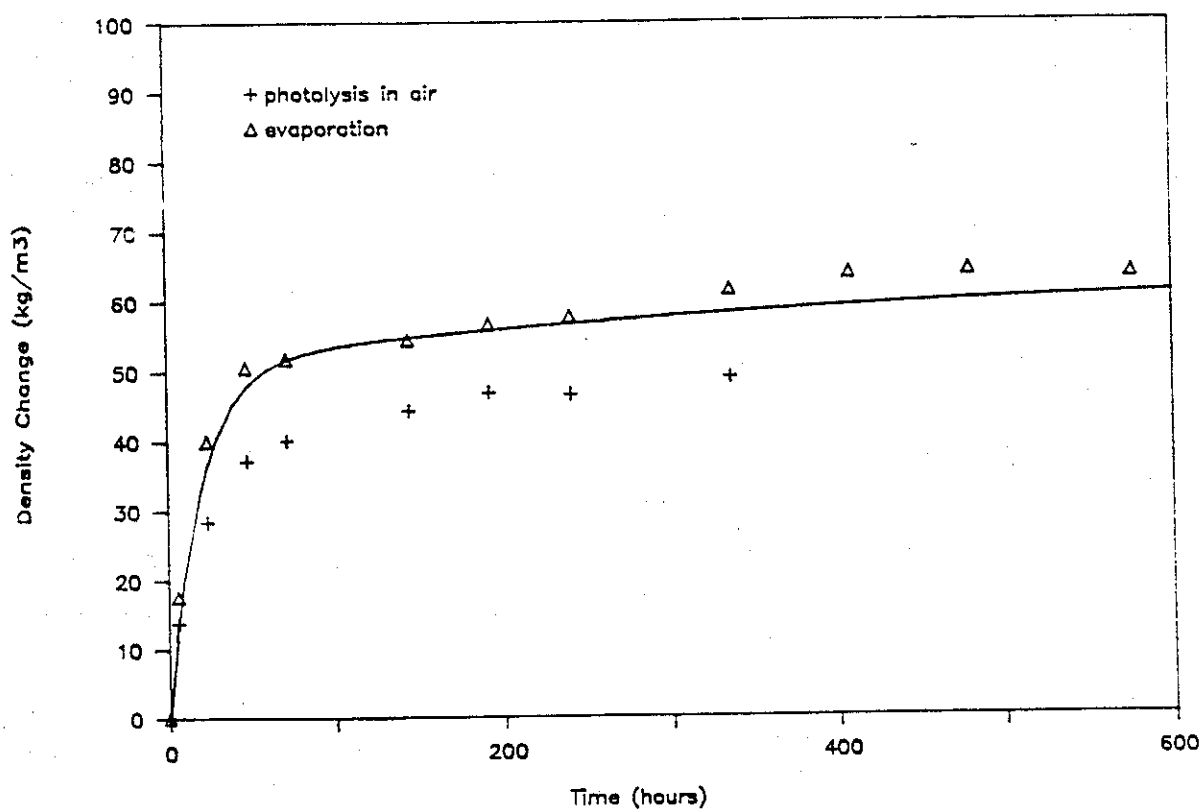


Figure 4.7 Effect of California Crude Oil API 15 exposed to photolysis.

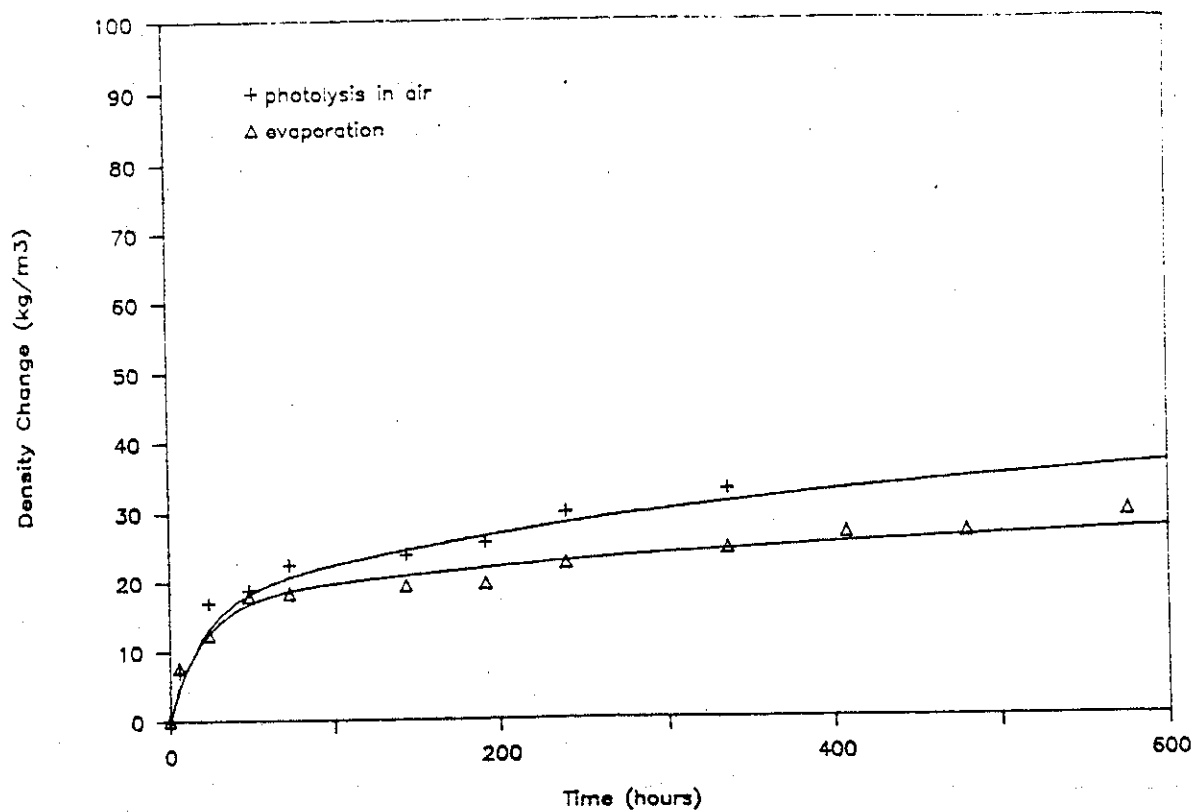


Figure 4.8 Effect of Cold Lake Bitumen exposed to photolysis.

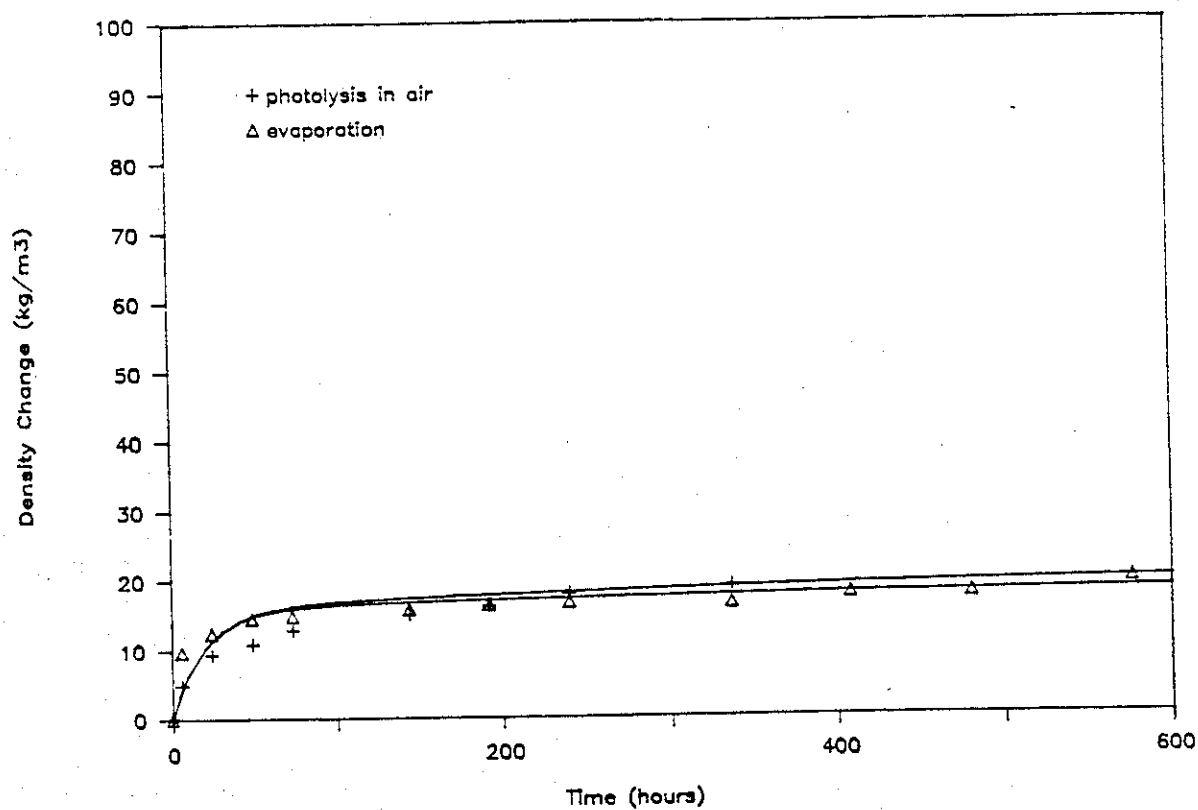


Figure 4.9 Effect of Bunker C Fuel Oil exposed to photolysis.

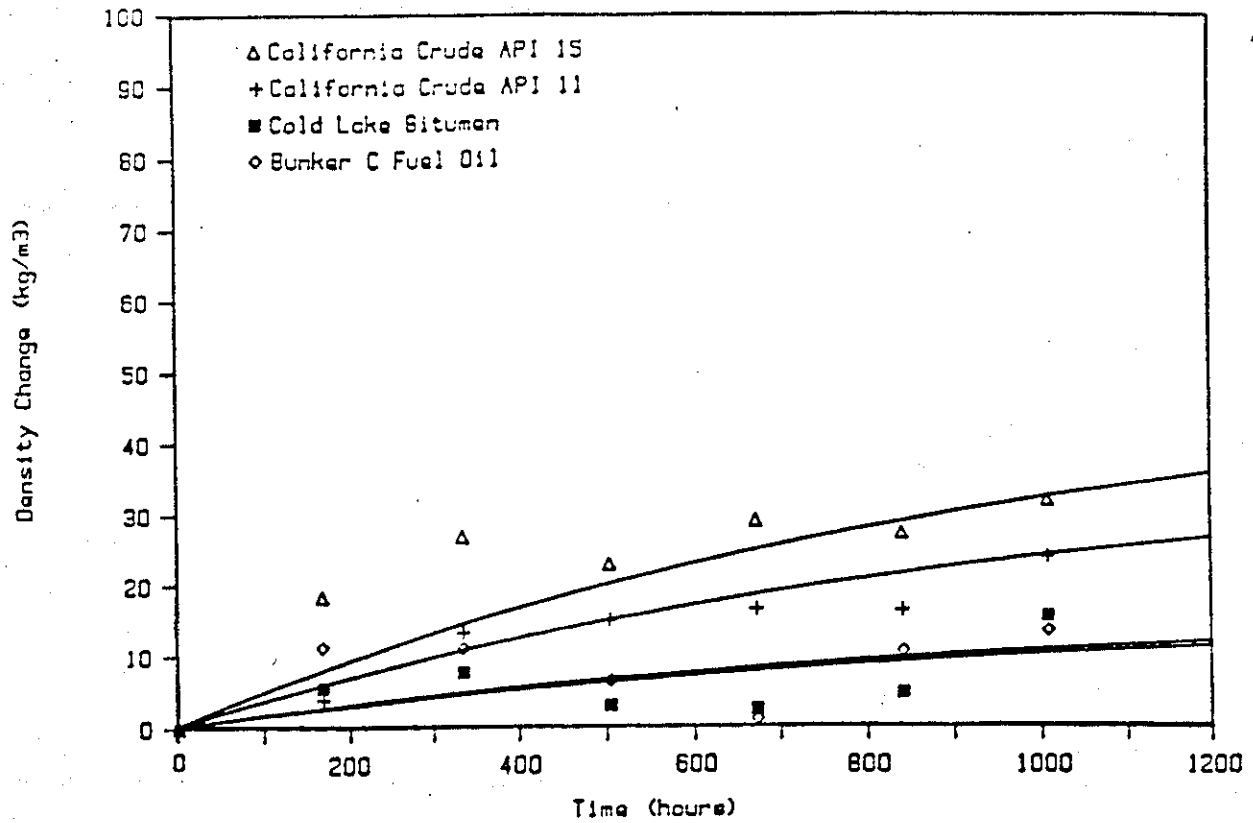


Figure 4.10 Dissolution in fresh water.

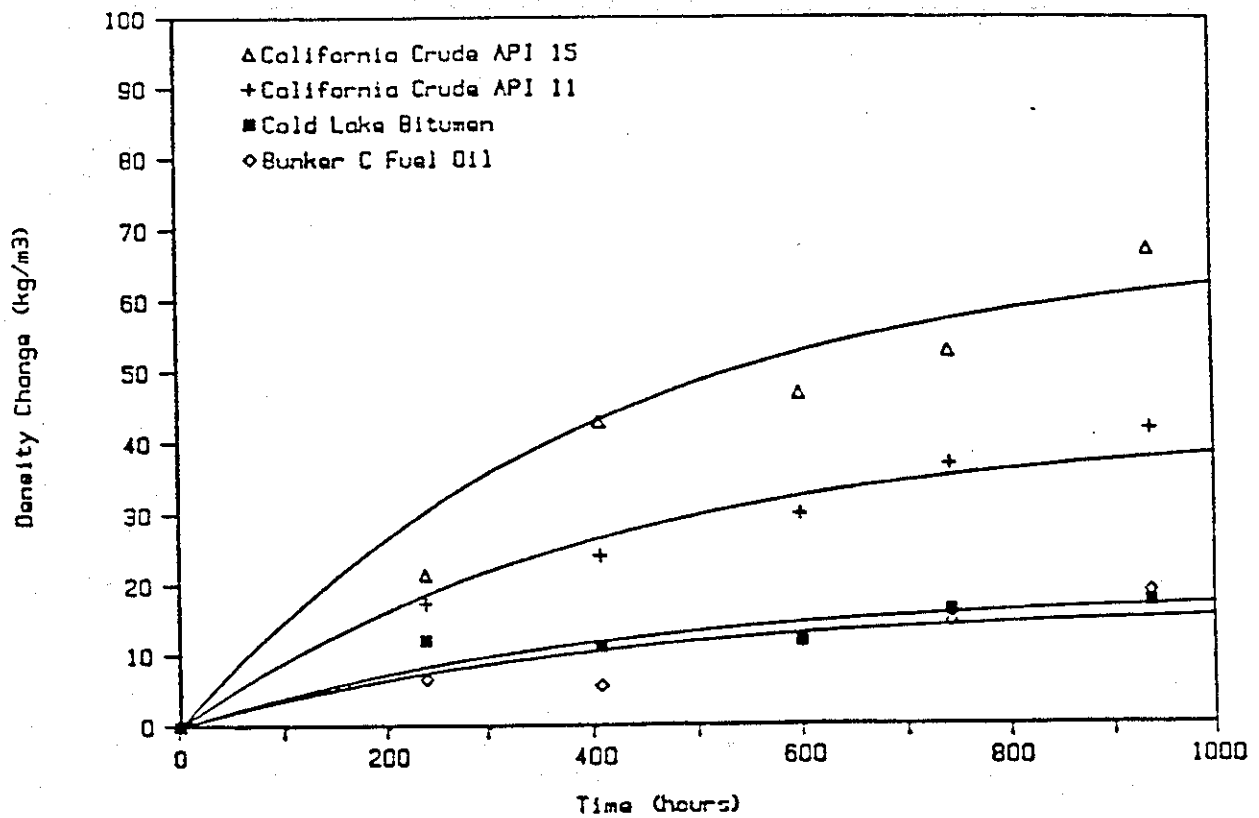


Figure 4.11 Dissolution in salt water.

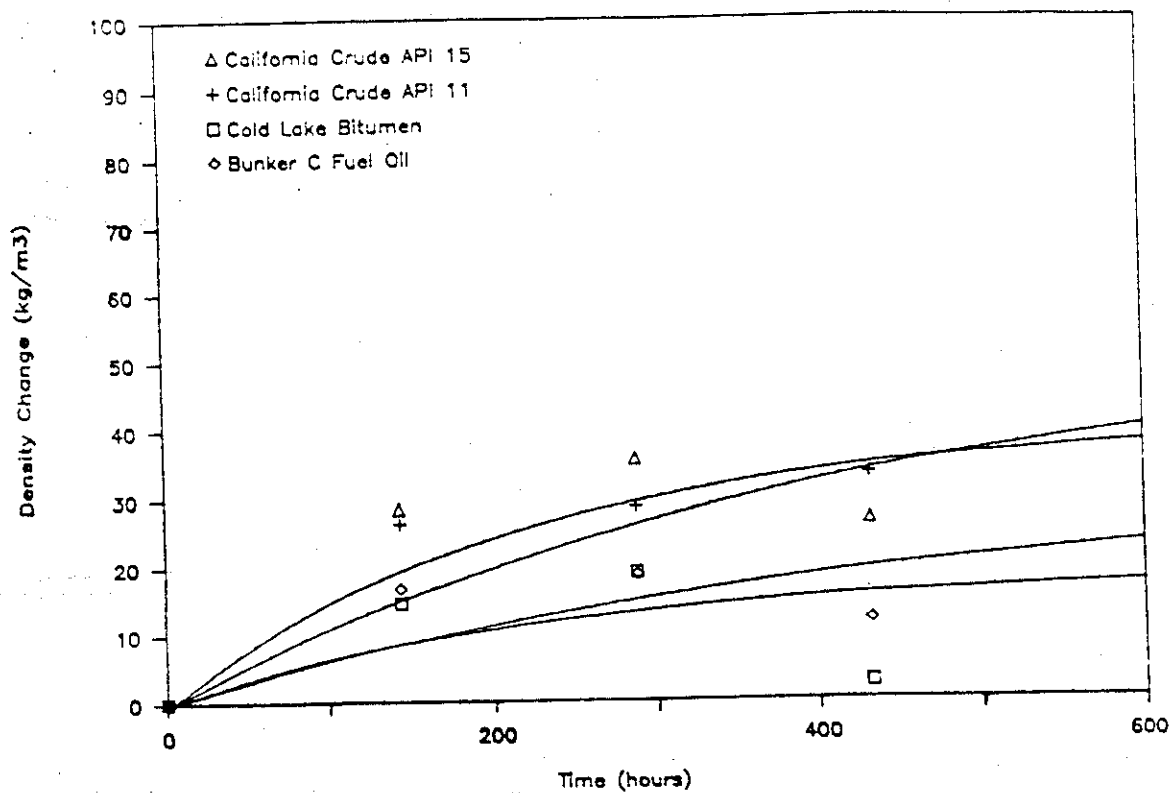


Figure 4.12 Photolysis in water.

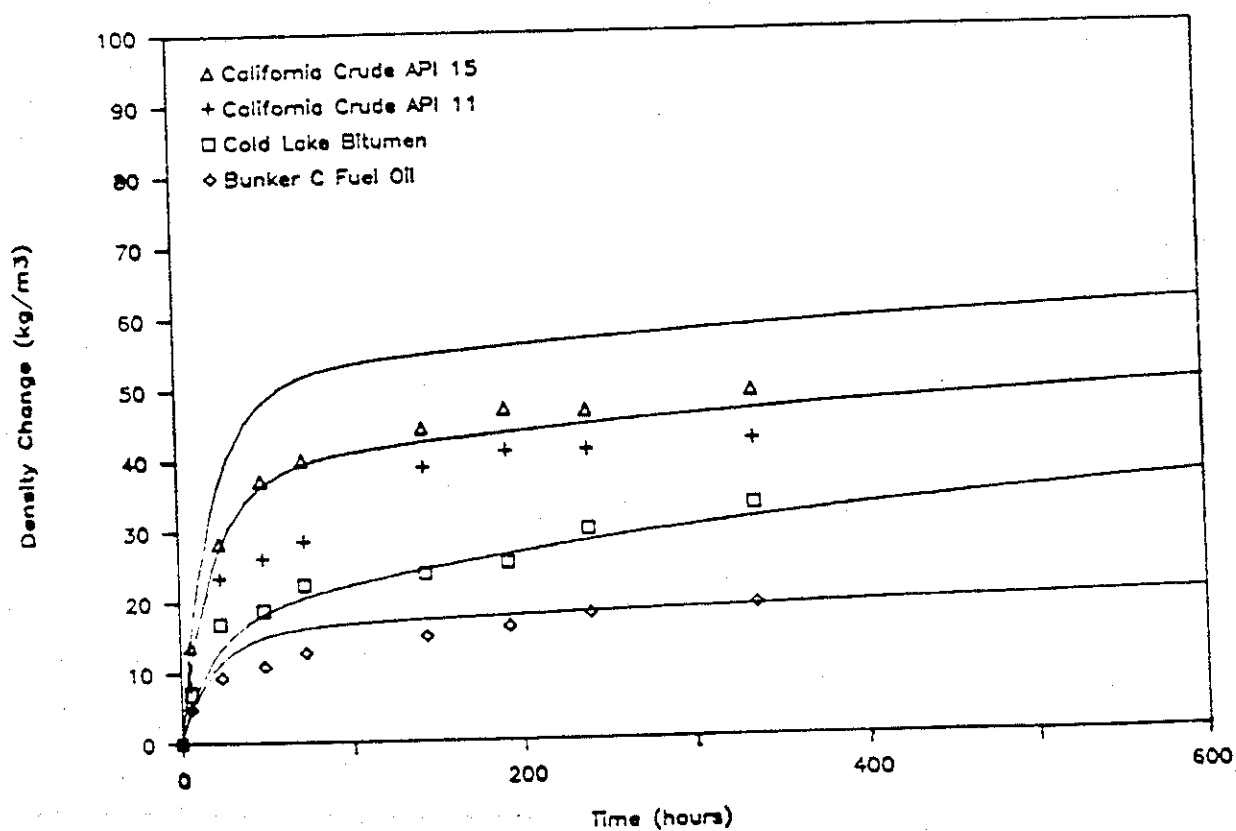


Figure 4.13 Photolysis in air.

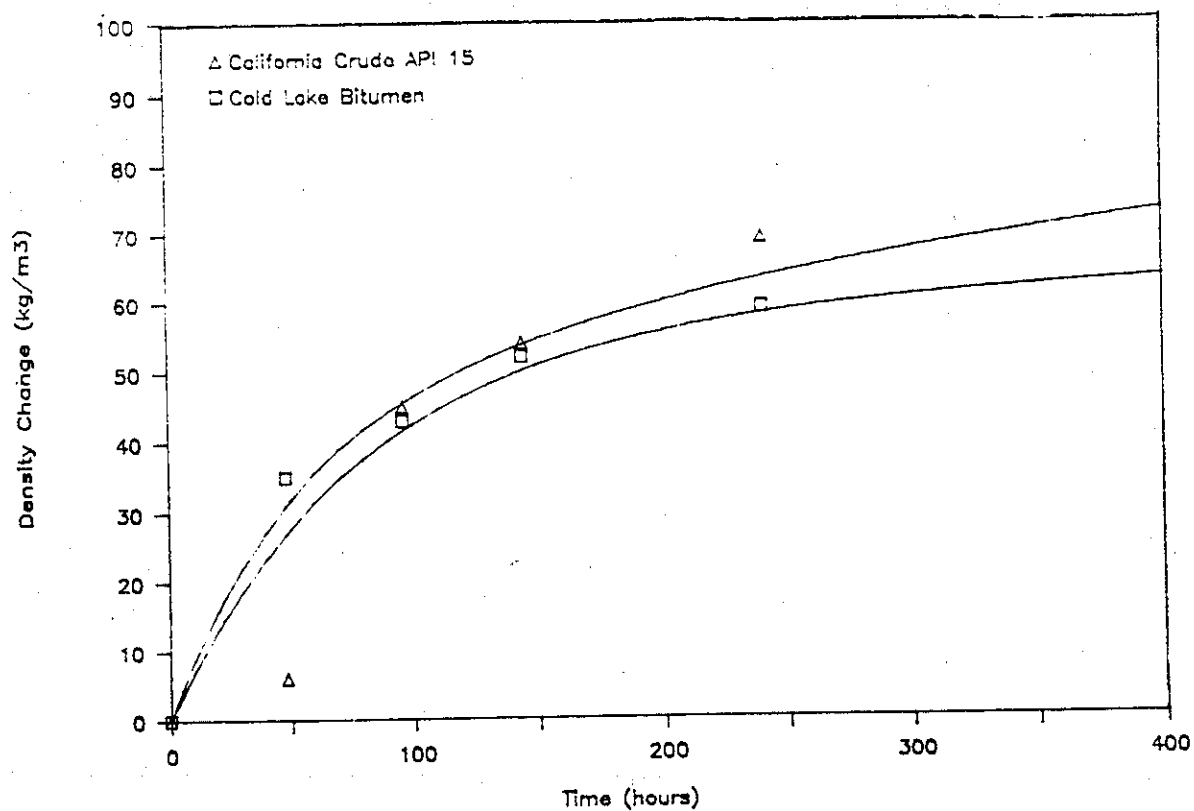


Figure 4.14 Effect of exposure of California Crude Oil API 15 and Cold Lake Bitumen to a suspension of Pottery Clay.

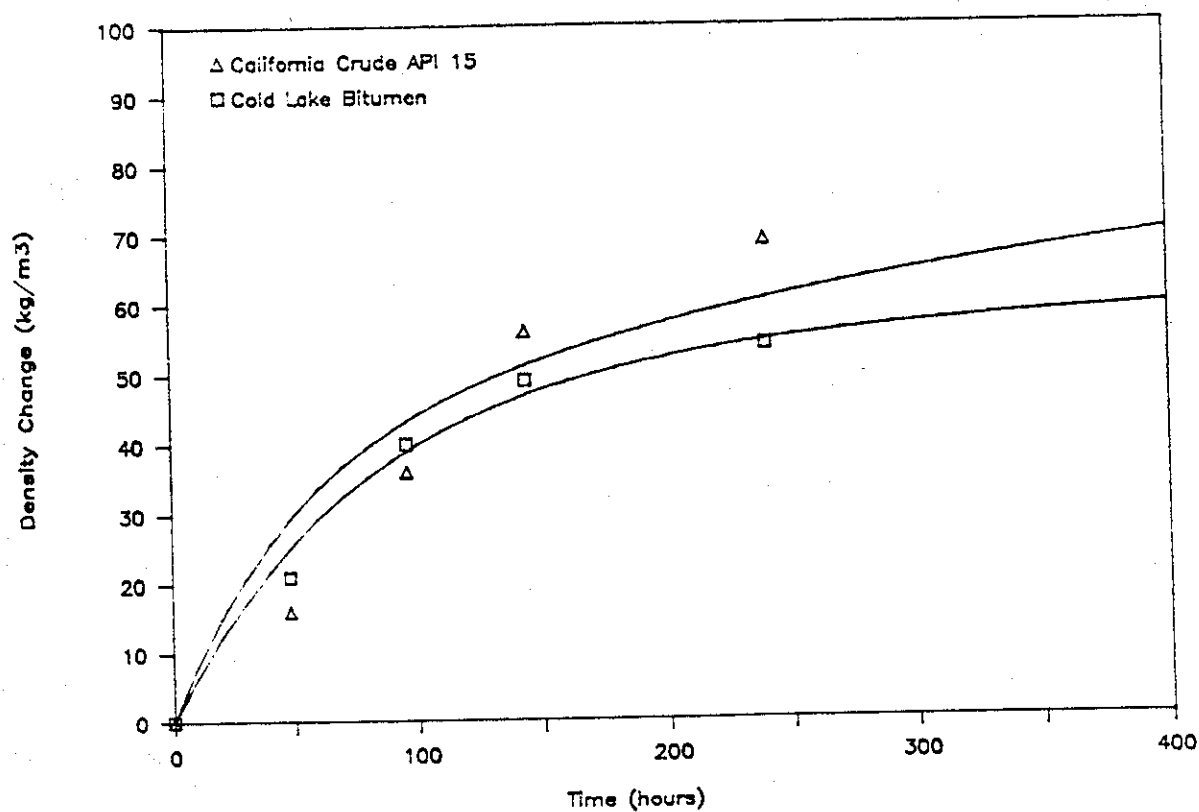


Figure 4.15 Effect of exposure of California Crude Oil API 15 and Cold Lake Bitumen to a suspension of Soapstone.



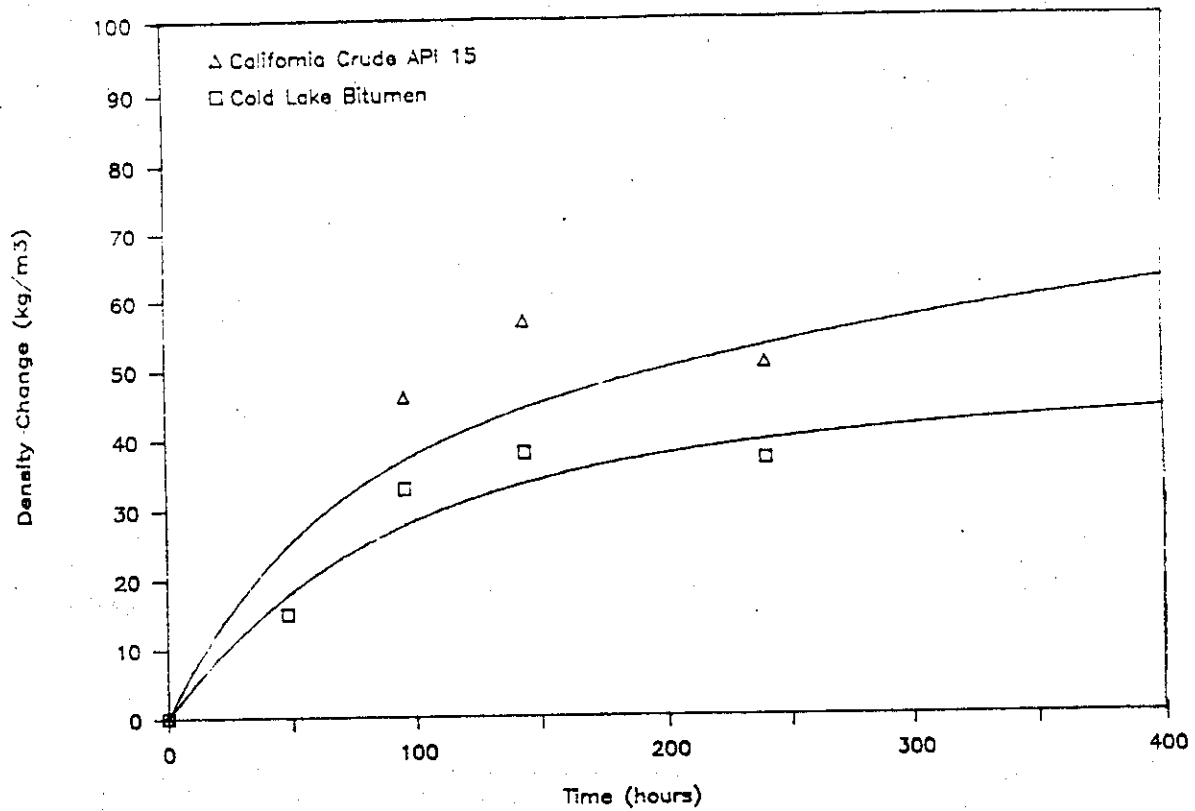


Figure 4.16 Effect of exposure of California Crude Oil API 15 and Cold Lake Bitumen to a suspension of Riverbed Clay.

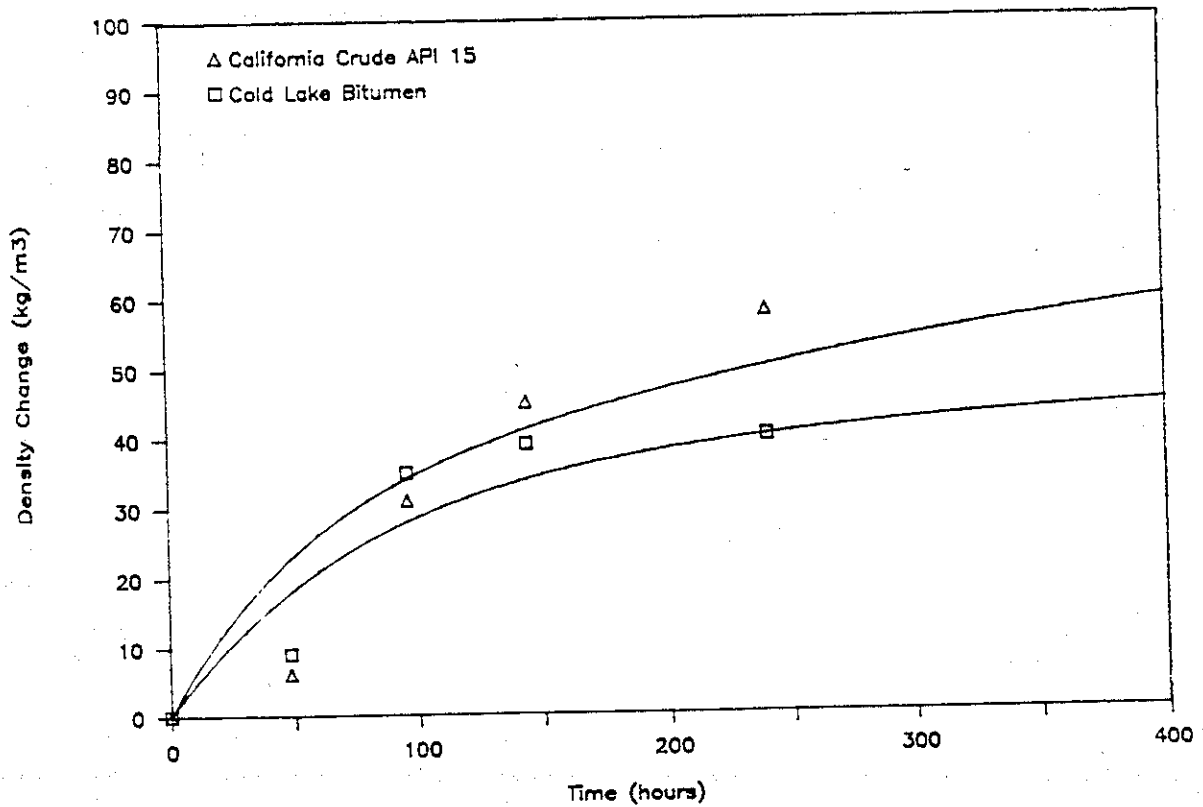


Figure 4.17 Effect of exposure of California Crude Oil API 15 and Cold Lake Bitumen to a suspension of Kaolinite.

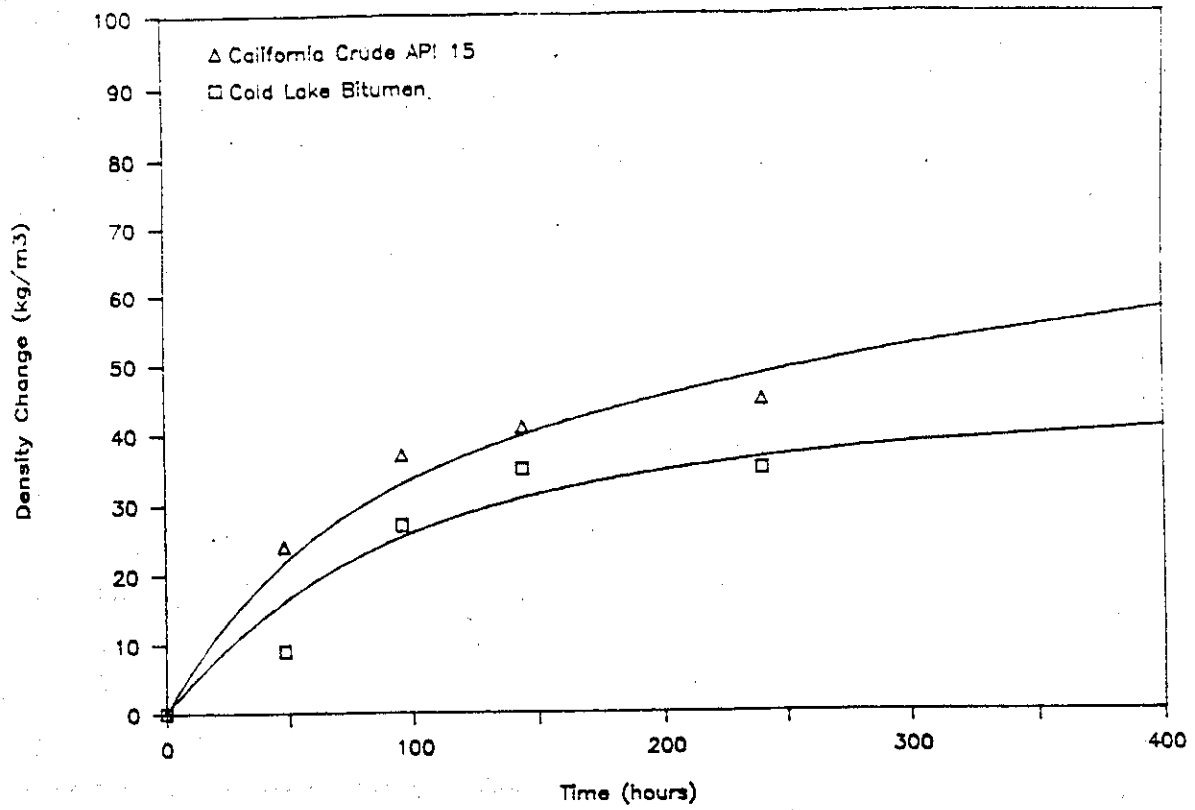


Figure 4.18 Effect of exposure of California Crude Oil API 15 and Cold Lake Bitumen to a suspension of Diatomaceous Earth.

## 5. DISCUSSION

### 5.1 Relative Magnitudes of Processes

For comparative purposes it is convenient to quantify the magnitude of the oil density increase attributable to each exposure regime after a period of approximately 10 days in the laboratory. This is regarded as about as long as is of interest under equivalent marine exposure conditions. At this stage it is convenient to assume that laboratory and oceanic times are equivalent, this issue being discussed in more detail later. It is likely that 10 day-old oil has either been stranded on shore or has been conveyed to some distant location. Also of interest is the oil density increase during the first two days in which the emergency response organizations will be treating relatively fresh oils. Accordingly in Table 5.1 the density increases attributable to each exposure regime are estimated for these two time periods. These quantities can then be used to estimate overall density increases, the resulting values being given in Table 5.1. These values in conjunction with the density increase equation thus provide a correlation of the available experimental data. The equation is relatively easily programmed for a personal computer and can be used to test oil density increases under a variety of conditions.

Table 5.1 Estimated Density Increases at Two Laboratory Exposure Times

#### at 2 days

<u>Oil</u>	<u>Do</u>	<u>Evap + Diss</u>	<u>Photolysis</u>	<u>Solids</u>	<u>Total</u>	<u>D</u>
C11	977.9	36.6	0	15.9	52.5	1030.4
C15	968.1	48.4	0	16.0	64.4	1032.5
CLB	985.1	17.1	1.37	14.3	32.8	1017.9
BC	971.2	15.1	0.23	14.5	29.8	1001

#### at 10 days

<u>Oil</u>	<u>Do</u>	<u>Evap + Diss</u>	<u>Photolysis</u>	<u>Solids</u>	<u>Total</u>	<u>D</u>
C11	977.9	44.8	0	25.6	70.4	1048.3
C15	968.1	56.9	0	25.8	82.7	1050.8
CLB	985.1	22.9	5.41	29.0	57.3	1042.4
BC	971.2	17.4	0.90	29.3	47.6	1018.8

Note: It is assumed that C11 oil behaves similarly to the C15 and BC to CLB for foreign matter attachment. Diatomaceous material is assumed.

The results indicate that the primary causes of oil density increase are (in order of decreasing magnitude) evaporation, incorporation of solid material, photolysis and dissolution. Conditions can arise in which singly or in combination will cause the oil to achieve a density exceeding that of sea water. Evaporation is particularly important for the crude oils which still retain some of the lower molecular weight hydrocarbons which are fairly volatile.

It is thus concluded that the potential exists for heavy oils to achieve density increases which will cause sinking in salt water. The key issue is "how long is this likely to take?" This issue is now discussed.

## 5.2 Incorporation into Oil Spill Models

In this section we discuss, in a rather speculative manner, methods by which laboratory exposure times could be translated into oceanic exposure times and the equations incorporated into oil spill fate models.

First, it should be possible to develop oil spill models or define expressions which characterise the status of oil masses at the sea surface. The oil could be characterised as a slick of defined thickness or as masses (blobs) with defined dimensions. A key obvious variable is the oil's area to volume ratio which is the reciprocal (approximately) of the oil blob or slick thickness. An oil of thickness 1 cm or 0.01 m thus has a specific area of  $200 \text{ m}^2/\text{m}^3$ , i.e. the sum of "top and bottom" surfaces.

Second, by observation, estimation, or using the equations suggested by Buist and Potter (1987) it should be possible to define the fractions of this area of  $200 \text{ m}^2$  which are exposed to evaporation (air) and dissolution (water). For a floating slick on a calm surface these will both be 0.5, but for periodically submerged oil masses the proportions could be, for example, 0.1 (air), 0.9 (water), i.e. 20 and  $180 \text{ m}^2/\text{m}^3$ . The laboratory exposure conditions are known because each oiled disk contained about  $1 \text{ cm}^3$  of oil which was spread to an area of about  $10 \text{ cm}^2$  giving a specific area of  $20 \text{ cm}^2/\text{cm}^3$  or  $2000 \text{ m}^2/\text{m}^3$ . It can be argued that similar extents of evaporation will occur in the laboratory in 1 day at  $2000 \text{ m}^2/\text{m}^3$  as will occur in 100 days at  $20 \text{ m}^2/\text{m}^3$ . This is the result of the area term in the basic mass transport equation. We can thus suggest an ocean surface to laboratory exposure time ratio of 100 for evaporation and  $2000/180$  or 11 for dissolution.

Obviously a correction should be applied for the effect of temperature on evaporation. The simplest procedure is to select a mean enthalpy of vapourization deduced from Trouton's Rule that the entropy of vapourization is typically 90 J/mol K. For a hydrocarbon of boiling point 150°C or 423K this corresponds to an enthalpy of vapourization  $\Delta H$  of approximately 38 kJ/mol thus  $\Delta H/R$  is approximately 4600 K and

$$P_2/P_1 = \exp(-4600(1/T_2 - 1/T_1))$$

A similar correction factor ratio could be defined (or estimated) for photolysis to relate solar radiation conditions at the sea surface to those in the laboratory.

For attachment of foreign matter the ratio should apply to the oil area in contact with the water and should include the ratio of the laboratory and ocean concentrations of foreign matter. The results suggest that increasing the concentration of foreign matter has the effect of increasing the rate of uptake, but not necessarily the final foreign matter content.

Finally, if an expression is available for water uptake to form water-in-oil emulsion or mousse, this could be included.

A brief computer program has been written in BASIC language which interrogates the user for the relevant oil properties and laboratory data (i.e. the density constants  $E_1$ ,  $E_2$  and the rate constants) then for the oceanic conditions on a daily basis. The density increase is then calculated for each desired time period (e.g. 6 hours). It is necessary to retain the prevailing density increase or laboratory exposure time during this calculation. A listing is given in the Appendix.

To illustrate the principle of the calculation we could consider oil which has been on the ocean surface for 4 days (96 hours) and has achieved exposure equivalent to 20 hours in the laboratory, i.e. the average (but not necessarily constant) exposure ratio has been 96/20 or 4.8. The density increase equation could be

$$\Delta D = 50(1 - \exp(-0.02t))$$

thus  $\Delta D$  at 20 hours is  $16.5 \text{ kg/m}^3$ . The next 6 hour period may have an exposure ratio of 5 thus a laboratory time of 1.2 hours, thus yielding a new overall exposure time to 21.2 hours and  $\Delta D$  to  $17.3 \text{ kg/m}^3$ , an increase of  $0.8 \text{ kg/m}^3$ .

This procedure has the advantage that changing environmental conditions can be included and the continuing increase in density estimated.

Figure 5.1 is an illustrative output from the computer program for a heavy crude oil showing six-hourly change in density of the oil as a result of exposure to hypothetical weathering conditions.

These results indicate that the issue of sinking requires the assessment of two separate aspects of oil spill behaviour.

First is an "equilibrium" consideration of whether or not processes have the potential to cause density increases to that of sea water. For many light oils this potential does not exist, but for oils of initial density above  $900 \text{ kg/m}^3$  it may exist. Evaporation and attachment of solids are the key processes. This aspect can be investigated in the laboratory since it is essentially an exercise in physical chemistry.

Second is a "kinetic" consideration of how long it will take for the potential to be realized. It is essentially a problem of relating oceanic and laboratory exposure times. The results shown in Figure 5.1 suggest that under real environmental conditions this factor is critically important. Few, if any, reliable observations of oil sinking have been reported. It is suspected that there are two reasons for this:

- (i) the extreme difficulty of making such observations which require underwater and preferably benthic viewing;
- (ii) in most spill incidents there is intense activity for about 10 to 20 days, after which time the oil slicks have reached shore, have been cleaned up, or have drifted far from the site of active observation. If it takes the oil 30 days to achieve a sinking density because of large ocean-to-laboratory exposure time ratios, it is unlikely that it will be observed at that time.

The first aspect can be investigated in the laboratory. The second requires oceanic observations supplemented by carefully designed experiments.

### 5.3 General Comments

The results obtained in this study are of course specific to the oils which were tested. However, it is believed that for other oils similar parameter values probably apply. It is possible that the experimental approach used here could be used to establish a protocol for the assessment of likely submergence behavior of specific oils. The oil characteristic which is most variable is probably the density increase attributable to evaporation. This can be relatively readily ascertained by exposing a volume of oil to evaporation in a wind tunnel or fume hood under conditions of known wind speed and film thickness. The oil can then be collected and its density measured. Alternatively distillation under controlled temperature conditions could be used.

An attractive alternative would be to "strip" a sample of oil with a slow nitrogen stream at controlled temperature conditions and collect the evaporated hydrocarbons by cryogenic trapping. This would ascertain the content of hydrocarbon which has the potential to evaporate. A similar approach could be used for dissolved hydrocarbons using a "generator column", but trapping the dissolved hydrocarbons from the eluate, possibly in an extracting solvent. These techniques are potentially much more sensitive than looking for changes in composition of the source oil. It is recommended that these approaches be investigated.

It is suspected that oil present in the near-surface region is subject to a "self-regulating" mechanism of density increase which will tend to cause it to adopt a density similar to that of the sea water. Evaporation will cause a density increase but only when the oil mass is exposed to air. There will also be active photolysis during daylight resulting in the formation of denser and more soluble hydrocarbons. There is often an accumulation of solid material at the turbulent water surface which will cause a further density increase. In total these processes will induce the oil to become denser, then sink. If the oil then passes into sea water of lower density it may be subject to sinking episodes and reach the benthic region. It is thus not surprising that heavy oils when exposed to marine environmental conditions often vanish from the sea surface for prolonged periods only to reappear in distant locations. Once submerged the oil may "stabilize" and be subject to only slight density changes.

The process of water in oil emulsion formation or "mousse" formation may also serve to increase the oil density, but in principle it is impossible for this process to cause the density to increase beyond that of sea water. Indeed for oils which have a density exceeding that of sea water, "mousse" formation will reduce the density.

A process which has not been considered in this work is that of dissolution of water in oil which may also cause a density increase approaching that of sea water. The magnitude of this effect is not known but it is believed to be slight.

As mentioned earlier, it is entirely possible that the solids incorporated into the oil are less dense than water, thus reducing the sinking tendency.

A compelling case can be presented for subjecting fuel oils or crude oils which are high in density to a rigorous determination of submergence characteristics in order that on-scene response groups can be warned about the probability of the oil displaying submergence behavior.

It is believed that this exploratory study has elucidated the dominant processes causing oil density increase and has established a basis for a protocol for a density increase assessment and a mathematical procedure for characterising these processes. This procedure could be incorporated with relatively little effort into existing oil spill models used for environmental assessment or for on-scene response purposes. Clearly further work is desirable to investigate the role of photolysis, better characterize evaporation process and study a variety of solid phases under various concentration conditions.



Figure 5.1 Illustration of Model Output. Specimen calculations showing density increasing to that of sea water in 78 and 210 hours.

Input parameter values

Fresh oil density	(kg/m <sup>3</sup> )	978
Water density	(kg/m <sup>3</sup> )	1024
Parameter E1	(kg/m <sup>3</sup> )	38
Parameter E2	(kg/m <sup>3</sup> )	15
Parameter TE1	(hours)	20
Parameter TE2	(hours)	400
Parameter TD1	(hours)	400
Parameter G	(kg/m <sup>3</sup> )	1
Parameter TP	(hours)	400
Foreign matter density	(kg/m <sup>3</sup> )	2000
Parameter ZF	(vol frn)	.03
Parameter TF	(hours)	60

Time increment (hours) 6

Time hours	Emulsion density	Parent oil density	Density increases due to				Water content percent	Fractional exposures to			Thickness solids	na
			evap&diss	photoly	solids	emulsion		air	water	photoly		
0.00	978.00	978.00	0.00	0.00	0.00	0.00	1.00	0.50	0.50	0.50	0.40	3.00
6.00	979.55	979.10	1.00	0.00	0.10	0.45	1.00	0.50	0.50	0.50	0.40	3.00
12.00	982.25	980.51	2.28	0.00	0.23	1.74	4.00	0.49	0.51	0.49	0.40	2.25
18.00	985.22	982.30	3.88	0.01	0.41	2.92	7.00	0.48	0.52	0.48	0.40	1.69
24.00	988.48	984.54	5.38	0.01	0.65	3.95	10.00	0.47	0.53	0.47	0.40	1.27
30.00	992.07	987.30	8.32	0.01	0.97	4.77	13.00	0.46	0.54	0.46	0.40	0.95
36.00	996.00	990.67	11.25	0.02	1.41	5.33	16.00	0.45	0.55	0.45	0.40	0.71
42.00	1000.24	994.67	14.66	0.02	1.99	5.57	19.00	0.44	0.56	0.44	0.40	0.53
48.00	1004.73	999.30	18.52	0.03	2.75	5.43	22.00	0.43	0.57	0.43	0.40	0.40
54.00	1009.35	1004.47	22.67	0.04	3.76	4.88	25.00	0.42	0.58	0.42	0.40	0.30
60.00	1013.94	1010.02	26.91	0.05	5.06	3.71	28.00	0.41	0.59	0.41	0.40	0.23
66.00	1018.29	1015.72	30.93	0.07	6.72	2.57	31.00	0.40	0.60	0.40	0.40	0.17
72.00	1022.23	1021.31	34.43	0.09	8.79	0.91	34.00	0.39	0.61	0.39	0.40	0.13
78.00	1025.64	1026.60	37.19	0.12	11.30	-0.96	37.00	0.38	0.62	0.38	0.40	0.10

\*\*\* Oil density exceeds that of water \*\*\*

## Input parameter values

Fresh oil density (kg/m<sup>3</sup>) 850  
 Water density (kg/m<sup>3</sup>) 1024  
 Parameter E1 (kg/m<sup>3</sup>) 50  
 Parameter E2 (kg/m<sup>3</sup>) 35  
 Parameter TE1 (hours) 40  
 Parameter TE2 (hours) 200  
 Parameter TD1 (hours) 100  
 Parameter G (kg/m<sup>3</sup>) 5  
 Parameter TP (hours) 30  
 Foreign matter density (kg/m<sup>3</sup>) 2500  
 Parameter ZF (vol frn) .02  
 Parameter TF (hours) 80

Time increment (hours) 6

Time hours	Emulsion density	Parent oil density	Density increases due to				Water content percent	Fractional exposures to			Thickness mm	
			evap&diss	photolv	solids	emulsion		air	water	photolv	solids	
0.00	850.00	850.00	0.00	0.00	0.00	0.00	1.00	0.50	0.50	0.60	0.30	3.00
6.00	852.84	851.11	0.95	0.10	0.06	1.73	1.00	0.50	0.50	0.60	0.30	3.00
12.00	859.41	852.55	2.19	0.23	0.13	6.86	4.00	0.49	0.51	0.59	0.30	2.25
18.00	866.28	854.41	3.79	0.39	0.23	11.87	7.00	0.48	0.52	0.58	0.30	1.69
24.00	873.50	856.78	5.82	0.59	0.37	16.72	10.00	0.47	0.53	0.57	0.30	1.27
30.00	881.14	859.60	8.40	0.84	0.56	21.35	13.00	0.46	0.54	0.56	0.30	0.95
36.00	889.24	863.87	11.61	1.15	0.81	25.67	16.00	0.45	0.55	0.55	0.30	0.71
42.00	897.81	868.21	15.54	1.52	1.14	29.60	19.00	0.44	0.56	0.54	0.30	0.53
48.00	906.84	873.80	20.25	1.95	1.59	33.04	22.00	0.43	0.57	0.53	0.30	0.40
54.00	916.26	880.35	25.72	2.44	2.19	35.91	25.00	0.42	0.58	0.52	0.30	0.30
60.00	925.91	887.76	31.82	2.96	2.99	38.15	28.00	0.41	0.59	0.51	0.30	0.23
66.00	935.55	895.81	38.30	3.48	4.03	39.74	31.00	0.40	0.60	0.50	0.30	0.17
72.00	944.89	904.14	44.80	3.97	5.37	40.75	34.00	0.39	0.61	0.49	0.30	0.13
78.00	953.66	912.35	50.89	4.38	7.08	41.31	37.00	0.38	0.62	0.48	0.30	0.10
84.00	961.67	920.12	56.23	4.68	9.20	41.55	40.00	0.37	0.63	0.47	0.30	0.07
90.00	968.91	927.35	60.72	4.86	11.76	41.56	43.00	0.36	0.64	0.46	0.30	0.05
96.00	975.52	934.22	64.54	4.96	14.72	41.30	46.00	0.35	0.65	0.45	0.30	0.04
102.00	981.66	940.98	68.03	4.99	17.96	40.68	49.00	0.34	0.66	0.44	0.30	0.03
108.00	987.37	947.69	71.45	5.00	21.25	39.68	52.00	0.33	0.67	0.43	0.30	0.02
114.00	992.53	954.06	74.80	5.00	24.26	38.47	55.00	0.32	0.68	0.42	0.30	0.02
120.00	996.95	959.60	77.93	5.00	26.67	37.35	58.00	0.31	0.69	0.41	0.30	0.01
126.00	1000.55	963.87	80.60	5.00	28.27	36.68	61.00	0.30	0.70	0.40	0.30	0.01
132.00	1003.38	966.72	82.61	5.00	29.11	36.66	64.00	0.29	0.71	0.39	0.30	0.01
138.00	1005.63	968.34	83.91	5.00	29.43	37.29	67.00	0.28	0.72	0.38	0.30	0.01
144.00	1007.53	969.11	84.60	5.00	29.51	38.42	70.00	0.27	0.73	0.37	0.30	0.00
150.00	1009.26	969.41	84.89	5.00	29.52	39.85	73.00	0.26	0.74	0.36	0.30	0.00
156.00	1010.92	969.50	84.98	5.00	29.52	41.42	76.00	0.25	0.75	0.35	0.30	0.00
162.00	1012.56	969.52	85.00	5.00	29.52	43.04	79.00	0.24	0.76	0.34	0.30	0.00
168.00	1014.19	969.52	85.00	5.00	29.52	44.67	82.00	0.23	0.77	0.33	0.30	0.00
174.00	1015.83	969.52	85.00	5.00	29.52	46.31	85.00	0.22	0.78	0.32	0.30	0.00
180.00	1017.46	969.52	85.00	5.00	29.52	47.94	88.00	0.21	0.79	0.31	0.30	0.00
186.00	1019.10	969.52	85.00	5.00	29.52	49.58	91.00	0.20	0.80	0.30	0.30	0.00
192.00	1020.73	969.52	85.00	5.00	29.52	51.21	94.00	0.19	0.81	0.29	0.30	0.00
198.00	1022.37	969.52	85.00	5.00	29.52	52.85	97.00	0.18	0.82	0.28	0.30	0.00
204.00	1024.00	969.52	85.00	5.00	29.52	54.48	100.00	0.17	0.83	0.27	0.30	0.00
210.00	1025.63	969.52	85.00	5.00	29.52	56.11	103.00	0.16	0.84	0.26	0.30	0.00

\*\*\*\* Oil density exceeds that of water \*\*\*\*

## 6. CONCLUSIONS

Four oils have been subjected to a novel, exploratory series of laboratory tests to investigate the potential for oil density increases to take place with the result that the oils may become appreciably submerged or even sink.

The most important density-increasing processes are evaporation and incorporation of foreign solid matter. The potential exists for these processes singly, or in concert, to cause oils to increase in density to that of sea water. A simple mathematical model has been assembled to calculate density increases. A personal-computer version is provided.

Whereas it is relatively straightforward to calculate density increase as a function of laboratory exposure time, it is difficult to relate this time to exposure times at the ocean surface.

It is believed that many heavy oils have the potential to sink but are not observed to do so because of the usual time-frame of observations, or because the oil is subject to stranding on shore or clean-up.

Recommendations are made for further research.

## REFERENCES &amp; BIBLIOGRAPHY

- Bobra, M.A. 1989. Photo-oxidation of petroleum. Proceedings of the 12th Arctic and Marine Oilspill Program, p. 129-148. Environment Canada, Ottawa.
- Buist, I.A. and Potter S.G. 1987. Oil Submergence. Spill Technology Newsletter, July-September 1987, pp. 65-82.
- Clark, B., Parsons, J., Yen, C., Ahier, A., Alexander, J. and Mackay, D. 1987. A study of factors influencing oil submergence. Report EE90, Environment Canada, Ottawa.
- Cook, F.D. and Westlake, D.W.S. 1976. Biodegradability of Northern Crude Oil. Department of Indian Affairs and Northern Development. Report No. QS-8116-000-EE-AI.
- Juszko, B.A. and Green, D.R. 1983. Sinking of Oil: Water Density Considerations. Spill Technology Newsletter, March-April 1983, pp. 22-26.
- Lichtenthaler, R.G., Hoag, W.R. and Mill, T. 1989. Photooxidation of probe compounds sensitized by crude oils in toluene and as an oil film on water. Environ. Sci. Technol. 23, 39-45.
- Mackay, D. and Shiu, W.Y. 1981. A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest. J. Phys. Chem. Ref. Data 10, 1175-1199.
- Mackay, D. 1987. Formation and Stability of Water in Oil Emulsions. Report EE93, Environment Canada, Ottawa.
- Mackay, D. and McAuliffe, C.D. 1988. Fate of hydrocarbons discharged at sea. Oil and Chemical Pollution 5, pp. 1-20.
- Meyers, P.A. and Oas, T.G. 1978. Comparison of associations of different hydrocarbons with clay particles in simulated seawater. Environ. Sci. Technol. 12, pp. 934-937.

Meyers, P.A. 1972. Association of fatty acids and hydrocarbons with numeral particles in sea water. PhD thesis, University of Rhode Island, Dept. of Oceanography, University Microfilms 73-16739, Ann Arbor, MI.

Seakem Oceanography Ltd. 1986. Oceanographic conditions suitable for the sinking of oil. Report EPS 3/SP/2, Environment Canada, Ottawa.

SL Ross Environmental Research Ltd. 1987. The transient submergence of oil spills: tank tests and modelling. Report EE96, Environment Canada, Ottawa.

Wilson, D., Poon, Y.C. and Mackay, D. 1986. An exploratory study of the buoyancy behaviour of weathered oils in water. Report EE85, Environment Canada, Ottawa.

Wong, C.S., Whitney, F.A., Cretney, W.J., Lee, K., McLaughlin, F., Wu, J., Fu, T. and Zuang, D. 1984. An experimental marine ecosystem response to crude oil and corexit 9527, Part I. Fate of chemically dispersed crude oil. Marine Environ. Res. 13, pp. 247-263.

## APPENDIX

## Computer Program for Calculating Oil Density Increase

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10 'PROGRAM TO ESTIMATE OIL DENSITY CHANGES ON WEATHERING
20 PRINT "Input oil characteristics by one of the following"
30 PRINT "Inputs to be user-specified - 1"
40 PRINT "The previously specified oil - 2"
50 PRINT "California API 11 - 3"
60 PRINT "California API 15 - 4"
70 PRINT "Cold Lake Heavy Crude Oil - 5"
80 PRINT "Bunker C Residual Fuel Oil - 6"
90 INPUT Q
100 ON Q GOTO 110, 240, 200, 210, 220, 230
110 INPUT "Fresh oil density eg 900 kg/m3 ":DO
120 INPUT "Evaporation/dissolution density parameter E1 eg 50
kg/m3 ":E1
130 INPUT "Evaporation characteristic time TE1 eg 50 h ":TE1
140 INPUT "Dissolution characteristic time TD1 eg 90 h ":TD1
150 INPUT "Evaporation density parameter E2 eg 50 kg/m3 ":E2
160 INPUT "Evaporation characteristic time TE2 eg 150 h ":TE2
170 INPUT "Photolysis density parameter G eg 10 kg/m3 ":G
180 INPUT "Photolysis characteristic time TP eg 40 h ":TP
190 GOTO 240
200 N$="California API 11":DO=978:E1=38:TE1=20:E2=15:TE2=400:
TD1=1000:G=0:TP=400:GOTO 240
210 N$="California API 15":DO=968:E1=51:TE1=20:E2=13:TE2=400:
TD1=1000:G=0:TP=400:GOTO 240
220 N$="Cold Lake Heavy Crude Oil":DO=985:E1=17:TE1=20:E2=13:
TE2=400:TD1=1000:G=12:TP=400:GOTO 240
230 N$="Bunker C Residual Fuel Oil":DO=971:E1=16:TE1=20:E2=3":
TE2=400:TD1=1000:G=2:TP=400:GOTO 240
240 'Oil properties are specified
250 LPRINT CHR$(15)
260 WIDTH "lpt1:",150
270 INPUT "Time increment for calculation eg 6 hours ":DTIM
280 INPUT "Water density eg 1024 kg/m3 ":DW
290 INPUT "Density of associating foreign matter DF eg 2000 kg/m3
":DFM
300 INPUT "Final volume fraction of foreign matter ZF eg 0.02
":ZF
310 INPUT "Foreign matter characteristic time TF eg 60 h ":TF
320 'Exposure conditions are specified
325 PRINT "Please wait while input data are printed"
330 LPRINT " "
340 LPRINT "Input parameter values "
350 LPRINT "Fresh oil density (kg/m3) "DO
360 LPRINT "Water density (kg/m3) "DW
370 LPRINT "Parameter E1 (kg/m3) "E1
380 LPRINT "Parameter E2 (kg/m3) "E2
390 LPRINT "Parameter TE1 (hours) "TE1
400 LPRINT "Parameter TE2 (hours) "TE2
410 LPRINT "Parameter TD1 (hours) "TD1
420 LPRINT "Parameter G (kg/m3) "G

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```

430 LPRINT "Parameter TP (hours) "TP
440 LPRINT "Foreign matter density (kg/m3) "DFM
450 LPRINT "Parameter ZF (vol frn) "ZF
460 LPRINT "Parameter TF (hours) "TF
470 LPRINT " " (hours) "DTIM
480 LPRINT "Time increment
490 LPRINT " "
500 PRINT " "
510 PRINT " "
520 TH=0:TL=0
530 THKL=.5
540 TLE=0:TLD=0:TLP=0:TLF=0
550 DEN=DO:DENEM=DO
560 DE=0:DP=0:DF=0:EM=0:FRA=0:FRW=0
570 LPRINT " Time Emulsion Parent oil Density increases
due to Water content Fractional exposures to Thickness"
580 LPRINT " hours density density evap&diss photoly
solids emulsion percent air water photoly solids
mm"
590 LPRINT " "
610 PRINT "Time is now (hours)";TH
620 PRINT "Current average oil thickness in millimetres eg 3
(formerly ";THK;") mm"
625 INPUT "Now ";THK
630 PRINT "New water content of emulsion (formerly ";EM;")
percent"
640 INPUT "Now ";EM
650 INPUT "Fraction of oil area exposed to air eg 0.5 ";FRA
660 FRW=1-FRA
670 PRINT "Fraction of oil area exposed to water is ";FRW
680 INPUT "Ratio of exposure to photolysis (ocean/lab) eg 0.5
";RP
690 INPUT "Ratio of exposure to foreign matter (ocean/lab) eg
0.5 ";RF
695 IF TH=0 THEN LPRINT USING"#####.##";TH,DENEM,DEN,DE,DP,DF,
DEM,EM,FRA,FRW,RP,RF,THK
700 QD=THKL*FRW/THK
710 QF=THKL*RP/THK
720 QF=THKL*RF*FRW/THK
730 QE=THKL*FRA/THK
740 TLE=TLE+DTIM*QE
750 TLD=TLD+DTIM*QD
760 TLP=TLP+DTIM*QF
770 TLF=TLF+DTIM*QF
780 DE=E1*(1-EXP(-TLE/TE1-TLD/TD1))+E2*(1-EXP(-TLE/TE2))
790 DP=G*(1-EXP(-TLP/TP))
800 DF=ZF*(DFM-DW)*(1-EXP(-TLF/TF))
810 DEN=DO+DE+DP+DF
820 DENEM=DEN+EM*(DW-DEN)/100
830 DEM=DENEM-DEN
840 TH=TH+DTIM
850 LPRINT USING "#####.##";TH,DENEM,DEN,DE,DP,DF,DEM,EM,FRA,
FRW,RP,RF,THK
855 IF DENEM > DW THEN LPRINT "**** Oil density exceeds that of
water ****"
860 PRINT " "
870 GOTO 610

```